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METHYLENE-BLUE AS INDICATOR IN DETERMINING THE TOXICITY OF PHENOL AND PHENOL-SALT SOLUTIONS TOWARDS YEAST

BY CHAS. G. FRASER

The following is an account of experiments in which yeast cells were poisoned by aqueous solutions of phenol with or without the addition of sodium chloride; in one series the ability to stain with methylene-blue was accepted as criterion of death, in the other the inability to form colonies on wort-agar. The composition of isotoxic solutions was found by direct comparison, using the two criteria of death; and the results of the two series were compared with those obtained in experiments on the distribution of phenol between the aqueous solutions and kerosene or toluene. The work was carried out at intervals during the winters of 1914 to 1918, whenever I could find time after my day's work to spend a few hours in the chemical laboratory; my thanks are due to Prof. W. Lash Miller for suggesting this research, and for encouragement to carry it through under such conditions

Apparatus and Technique

The Stock Culture. Pure cultures of *Saccharomyces cerevisiae race F* were prepared as follows: A piece of the size of a pin-head taken from the centre of a fresh Fleischmann's yeast cake was shaken up with 10 cc sterile wort and diluted with wort as described below until one cc contained about 25 to 100 cells. One cc of this suspension was added in a test-tube to 10 cc melted wort-agar, shaken, and poured on a petri dish which was covered inverted and placed in a thermostat at 25° C. In 48 hours the colonies are about the size of pin heads; in 4 days they have a diameter of about 3 mm. One colony from such a plate was transferred to 10 cc wort with a sterile platinum loop, diluted, etc., as before, and a second series of plates prepared as just described;

the usual precautions against access of foreign forms being observed. Such a set of plates served as stock cultures; they could be kept at room temperature for about a fortnight.

From one of them, about 24 hours before cells were wanted for an experiment, 10 cc wort was inoculated and placed in a thermostat. The yeast was thus experimented with when fermentation was at its highest; the cells were hyaline in appearance, oval in form, and not clumped together. Such a preparation is referred to hereafter as "wort culture;" its "count" was usually somewhere round 250.

Wort-free Cells.—After attempts to isolate the cells by means of a centrifuge, filtration was adopted. A circle of filter paper was sterilized by soaking in absolute alcohol and laid on the plate of a sterilized Buchner funnel connected with the pump; 25 to 50 cc of wort culture, depending on the "count" was poured on the centre of the paper in a thin stream from a pipette; the liquid went through and the cells remained in one spot, they were removed by a sterilized spatula and suspended in the requisite amount of distilled water usually half the volume of the wort culture used.

In the poisoning experiments, a measured volume (usually 5 cc) of this suspension was then added to the poison liquid (usually 45 cc, sometimes less) previously brought to 25° C in the "rocker tube." Blank experiments showed that the cells can remain in distilled water without harm much longer than is necessary for this manipulation.

Preparation of the Wort.—Distillers' malt of diastase index 180 was freshly ground in a coffee mill, and 250 g of it (about 600 cc) put in a two-litre flask with 700 cc distilled water; the neck of the flask was closed with a wad of absorbent cotton, and it was kept for 24 hours in a water bath at 60–65° C. The contents were then filtered hot through cotton fabric, giving a straw colored filtrate, which was filtered again through paper; this second filtration took about 12 hours (over night) and yielded about 500 cc of a red-brown liquid of sp. gr. 1.07. The mouth of the flask containing the filtrate was

closed tightly with a wad of cotton, and the contents "autoclaved," at 15 lbs. pressure (120° C) for 15 minutes; on cooling, the liquid was found to be still darker in color and to contain a flocculent whitish precipitate. This precipitate kept on forming for about three days at room temperature, after which the liquid was filtered through filter paper into the tubes and flasks in which it was to be used. These were closed with cotton wool and "Arnoldized," i. e., heated in steam in the autoclave at atmospheric pressure for 20 minutes each time on two successive days.

Preparation of Wort-agar.—Ten grams agar-agar, cut into short lengths with scissors, was washed in a bowl for 30 seconds with tap water at 60° C, the water drained off, and the agar introduced into a two-litre candy jar, using a glass lamp shade as funnel. To this was added 500 cc of wort; the mouth of the jar was covered with the lid of a petri dish, and the contents autoclaved for 25 minutes at 120° C. The liquid was then filtered through absorbent cotton in a hot water funnel and "tubed," i. e., collected in portions of about 10 cc in test-tubes, which were then wadded, Arnoldized, and cooled. When required for plating, the wort-agar was melted by immersing the tube in water at about 90° C, cooled, and kept ready in a water bath at 38° C. Its jellying point was about 25–30° C.

The Thoma Chamber, and the "Count." The Thoma chamber, or haemocytometer with Thoma ruling, is a small glass cell covered by a cover-glass 0.1 mm from the bottom of the cell; the latter is ruled into 16 squares each of which encloses 16 smaller squares 0.05 × 0.05 mm in area. The liquid over each of these small squares thus occupies 25×10^{-8} cc. A drop of the suspension of cells to be counted was examined in the chamber with a low power and a representative group of small squares found; a magnification of 430 was used for the counting, and the number of cells over 16 small squares, i. e., in 4×10^{-6} cc, recorded as the "count." Thus a count of 1 corresponds to 250,000 yeast cells per cc.

The cells are ellipsoidal and average 0.0006 cm in length

by 0.0004 in width; the sp. gr. of yeast is about 1.1. Thus a count of 1 corresponds to 3.75×10^{-6} gram yeast per cc. This conclusion, which, of course, hangs on the assumed average size of the cells, was checked by suspending 0.20 g from a yeast cake in 100 cc water; the count proved to be 50, which according to the foregoing calculation corresponds to 0.187 g yeast cells.

For microscopic examination (430 diam.) a "dense" suspension with a count of about 50 is convenient, whereas for plating a "sparse" suspension holding about 100 cells per cc—i. e., with a count of 0.0004—is best. The dense suspension thus contains about 125,000 times as many cells as an equal volume of the sparse and to prepare a plate from a dense suspension recourse must be had to repeated dilution; if the "machine"[1] be used, one loopful (0.005 cc) introduced into 100 cc water gives a liquid of which 0.2 cc is sufficient for the plate.

Thermostat Rocker.—After preliminary experiments with glass stirrers, rotating bottles, etc., the following apparatus was devised; it keeps the liquids thoroughly stirred and the temperature constant, yet samples can be removed conveniently and quickly without allowing access to foreign organisms. A number of glass tubes, about a foot long and one inch in diameter, closed at one end, are bent at right angles in the middle, and fastened by clips of spring brass to a frame; the latter is supported in the water of a thermostat and rocked to and fro by a motor, about 30 times a minute, through an angle of 50°. The lower, closed, end of each tube has a capacity of about 75 cc, so that up to 50 cc of liquid can splash about easily and keep well stirred; the upper ends stay above the water level, and are closed by cotton wool; to remove a portion for examination, a sterile pipette is inserted between wool and glass.

Toxicological Equivalents (Methylene-Blue)

Details of a Determination.—The object of the following

[1] Jour. Phys. Chem., **24**, 564 (1920).

experiments was to find the amount of phenol that must be contained in 100 cc of a solution containing 5 g sodium chloride, if the solution in question is to be isotoxic with a solution containing 0.60 g phenol and no salt in 100 cc.

Preliminary experiments having given the approximate composition of the solution sought, six solutions, *a*, *b*, *f*, were made up of such compositions that when 5 cc water was added to 45 cc of each of them they would contain, respectively: (*a*) no salt and 0.60 g phenol per 100 cc, or for short 0–0.60, (*b*) 2.0 g salt, 0.45 g phenol per 100 cc, or 2.0–0.45, (*c*) 2.0–0.49, (*d*) 2.0–0.51, (*e*) 2.0–0.52, (*f*) 2.0–0.55. Forty-five cc of each was placed in a rocker tube and brought to 25° C; to each was then added 5 cc of a suspension of yeast cells in distilled water, free from wort, and the time was noted. At measured intervals of time, one cc portions were removed from the tubes in turn, added to 1 cc methylene-blue 0.03% and a drop examined under the microscope. The quickest way to determine the percentage of cells stained is to count the cells, until the number one hundred has been reached, making a mark in the note book whenever a blue one is counted; for this determination a Thoma chamber is not necessary, though convenient. Even in the case of the strongest poisons used, the dilution to one-half, consequent on adding the dye, slows the action sufficiently. In order that the weight of yeast in the solution might be as small as possible in comparison with that of the phenol, the cell suspension was made up to give a count of 10 to 20 after poison and stain had been added; and in order to save time, a fairly high concentration of methylene-blue was used in the stain, but as the examination took only one minute, there was no danger of the dye acting as a poison.

The results are given below, arranged in the order of toxicity of the solutions. They leave no doubt that a solution containing 2.0 g salt and 0.53 or 0.54 g phenol in 100 cc would "kill" the cells at the same rate as 0.60% phenol in water.

2—.45		2—.49		2—.51		2—.52		0—.60		2—.55	
Min.	%	Min.	%	Min.	%	Min.	%	Min.	%	Min.	%
7	7	5	5	3	7	5	12	1	15	1	15
20	15	13	18	8	30	12	28	7	28	6	63
32	30	27	28	24	50	21	44	9	37	10	90
38	40	36	60	35	100	25	65	15	68	12	100
46	75	43	95			30	100	20	80		
52	90							23	100		
55	100										

Results.—The following table gives the compositions of toxicologically equivalent solutions determined as described above:

	Percent Phenol					
No salt	0.50	0.55	0.60	0.65	0.70	0.75
2% salt	0.45	0 49	0.53	0.58	0.61	0.66
5% salt	0.37	–	0.45	—	—	0.55

Toxicological Equivalents (Plating)

In these experiments the cells were poisoned as described in the preceding section, but instead of determining the moment of death by staining, 1 cc from the rocker tube was added to 10 cc wort-agar and plates were poured. The results did not come out as I anticipated, so a great many determinations had to be made before hitting on the solutions containing salt which were isotoxic from this point of view with the six solutions of phenol in water used as standards of reference. In every case comparison was made between plates from tubes which had been put in the rocker at the same time and seeded from the same yeast suspension. The following are the results so obtained:

	Percent Phenol					
No salt	0.50	0.55	0.60	0.65	0.70	0.75
2% salt	0.40	0.44	0.49	0.52	0.57	0.62
5% salt	0.28	0.33	0.38	0.42	0.45	0.48
10% salt	—	—	0.18	0.21	0.24	0.26
75% salt	0.08	0.09	0.12	0.14	—	0.18

Phenol and salt of the concentrations at which they are present in the wort-agar (viz., one-eleventh of their concentrations in the rocker tubes) are not toxic to yeast and do not prevent the growth of normal cells. At the time these experiments were carried out, this was thought sufficient; but in view of the results with methyl-green, the influence of these traces on the growth of colonies evidently needs investigation, and the necessary experimental work will be undertaken next winter.

Chemical Equivalents (Toluene and Kerosene)

I made a large number of equilibrium determinations using kerosene as immiscible liquid, and analyzing the aqueous layer only. A wholly independent set was made by Mr. Fulmer, using toluene; both sets were carried out at 25° C in the manner described by Prof. Lash Miller.[1] The chemical equivalents calculated from these two sets agreed within 0.015 with the average of the two, which is here given for rounded concentrations of phenol in water. The numbers in each horizontal line form an arithmetical progression. Prof. Miller's determinations for solutions containing 2% salt are 0.01 higher than those given here; Mr. Laird's (whose calculation involved an extrapolation) are 0.02 higher.

	Percent Phenol					
No salt	0.50	0.55	0.60	0.65	0.70	0.75
2% salt	0.44	0.485	0.53	0.575	0.62	0 665
5% salt	0.37	0.405	0.44	0.475	0.51	0.545
10% salt	0.265	0.29	0.315	0.34	0.365	0.39
15% salt	0.20	0.22	0.235	0.25	0.27	0.29

Comparison of Equivalent

Comparison of the three sets of equivalent solutions shows that if staining by methylene-blue be adopted as criterion of death, solutions of phenol in water are equally toxic with their chemical equivalents containing salt; but that if

[1] Jour. Phys. Chem., **24**, 564 (1920).

absence of colony-formation on wort-agar be adopted as criterion of death, the solutions containing salt are the more toxic. The accompanying figure has been designed to bring out these relations; in it the abscissae give the number of grams phenol in 100 cc of the poison, the number of grams salt are entered on each curve. The results of the determinations of chemical equivalents are indicated by circles; the ordinate of each gives the number of grams phenol in 100 cc of a phenol-kerosene solution in equilibrium with the aqueous solution whose composition is given by abscissa and line

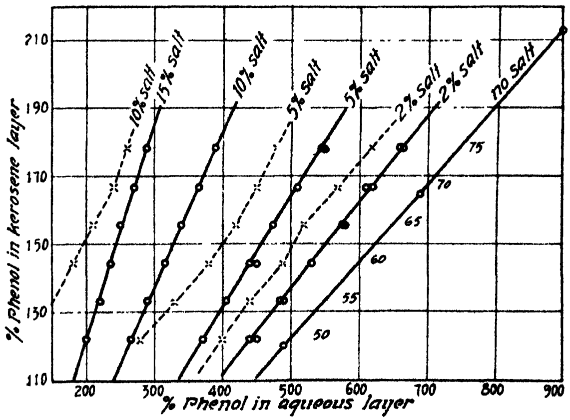

Fig. 1

number. The results of the poisoning experiments are indicated by dots (meth.-blue) and crosses (plating); the abscissa gives the percentage of phenol in the poison, but the ordinate is the ordinate of the phenol-water solution with which the solution represented is equally toxic, and, of course, is different for the two criteria of death. Dots and circles fall on the same curves—chemically equivalent solutions are isotoxic (meth.-blue). Crosses fall on a curve to the left—salt increases the toxicity (plating) more than it increases the potential of the phenol.

In view of my own experiments with methyl-green, and of Mr. Fulmer's work with ammonium fluoride (which will

shortly be published), and of the general belief that "emaciated" cells will not form colonies on agar, it seems likely that many cells reported "dead" by the plates were not dead but sleeping. In any event it is clear that acquisition of the power to stain marks a very definite point in the progress of necrosis; and while the time it takes to bring this stage of death about depends on the peculiarities of the individual yeast cell, yet for each one of them it depends only on the temperature and on the chemical potential of the phenol in the solution employed. Inability to grow in wort-agar seems to mark an earlier stage; the time it takes to reach that stage evidently depends on some other factor than the two which govern the acquisition of the power to stain; the osmotic pressure of the toxic liquid may have something to do with it. Replacement of wort-agar by other media would undoubtedly lead to other data, and by their use milestones could be marked along the road to death, and the rates of loss of vitality and of recovery could be followed quantitatively.

Summary

Solutions containing phenol and sodium chloride, of such compositions as to be in equilibrium with the same solution of phenol in toluene or in kerosene, are isotoxic towards yeast if the ability of the cells to stain with methylene-blue be adopted as criterion of death. If inability to form colonies on wort-agar be adopted, the solutions containing salt are the more toxic.

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THE EFFECT OF ALCOHOL ON THE TOXICITY OF PHENOL TOWARDS YEAST

BY ELLIS I. FULMER

In the earlier experiments of Mr. Fraser, and in some of my own, it became disagreeably apparent that yeasts, derived originally from the same cell and grown in wort from the same bottle, might show very different degrees of resistance to phenol. Examination of the note-books showed that in such cases the poison liquids had been seeded with yeast from wort-cultures of very different ages. This led to a systematic measurement of the resistance towards 0.66% phenol of cells taken from the wort at different stages of the fermentation, and to the identification of the more resistant forms with the "resting cells" already studied by many authors, and to a convenient recipe for the preparation of yeast cells by means of which this source of variation is eliminated. The toxicity of phenol solutions containing alcohol was then studied, both by plating and with methylene-blue; the chemical equivalents of the solutions used were determined by shaking out with toluene; and the results of the three series of determinations were compared. This work was carried out in the winter of 1917–1918, under the direction of Prof. W. Lash Miller; I am glad also to acknowledge my indebtedness to Mr. C. G. Fraser who initiated me into the unfamiliar technique.

When wort is seeded with yeast, the first evidence of fermentation is the formation of white flecks of foam on the surface, whereupon if the flask be shaken effervescence ensues. The time at which these flecks appear is quite definite, and may easily be determined within half an hour; if the wort had been seeded to a count[1] of 2 or 3, the count at this point will be about 50. The second stage is that of active fermentation; and in the third the fermentation grows slower and finally ceases. In the first and second stages the cells

[1] 2 or 3 times 250,000 cells per cc.

are hyaline in appearance, not granular, vacuoles are not prominent, and the cell-wall is hardly visible; in the third stage they become granular and vacuolate, and under the microscope the cell-wall appears as a thick line.

These latter are the "resting cells." Hansen[1] found that yeast taken from a culture two days old was killed in five minutes by immersion in water at 56° C, whereas if taken from a culture two and a half months old, five minutes in water at 60° C was needed. Kayser[2] who confirmed and extended these observations, pointed out that the "resting cells" are in many respects half-way between vegetative cells and spores, which latter are resistant to many unfavorable conditions.

Addition of alcohol to the wort before seeding with yeast, hastens the formation of these resting cells; this method is employed in the wine industry to preserve "must" in an unfermented condition. Experiments of my own in which 4% or 10% by volume of alcohol was added to the wort gave cells abnormally resistant to phenol in from 3 to 7 hours instead of in 26 hours; when 16% of alcohol was added, however, all the cells were dead in 7 hours.

The progress of the fermentation of 100 to 200 cc wort was followed (in an 800-cc Erlenmeyer flask, to avoid loss by foaming when shaken), determining the loss of carbon dioxide by weighing (to one centigram) from time to time, and the corresponding "staining-time" of the cells, i. e., the time of immersion in 0.66% phenol required to render all the cells stainable by 0.05% methylene-blue. The flask was thoroughly shaken before each weighing to overcome supersaturation; a correction of 0.0112 g per hour to allow for evaporation was arrived at by experiments in which no yeast had been added to the wort. As the undesirable "resting cells" are abnormally resistant to phenol, determination of the "staining-time" serves as a convenient method both of

[1] Jorgensen: Microörganisms and Fermentation.

[2] Ann. Inst. Pasteur. 3, 539 (1889).

detecting their presence, and of comparing the resistance of the worst of them with that of normal cells.

The following table gives the result of a typical run with 100 cc wort, seeded with yeast to a count of 2 to 3, and kept at 25° C during the fermentation.

Time	4	9	23	26.5	51.5	73	103 hours
CO_2	0.02	0.17	2.71	3.37	6.06	6.32	6.62 grams
St. T.	25	23	24	25	120	121	— min.

A number of such runs was made, with different amounts of wort, seeded to various counts with yeast from the same stock; in every case when the weight of carbon dioxide evolved was ess than 4.0 g per 100 cc wort, the staining-time was found to be 25 ± 2 minutes, while

for CO_2 evolved	4.13	4.70	6.06	6.34 g per 100 cc wort
St. T. was found	52	79	120	121 minutes

Measurements by Mr. N. Clark, which showed that, until the loss of carbon dioxide reaches 4% of the weight of the wort, the rate of reproduction of the yeast follows the logarithmic law, furnish further evidence of the uniformity of the cells during that period of the fermentation.

From these results a recipe for the production of "normal" cells has been deduced which has been used in all our subsequent work. It is: Using wort and yeast prepared as described by Fraser,[1] seed the wort to a count of 2 or 3, keep at 25° C, and use within 24 hours.

The Effect of Alcohol on the Toxicity of Phenol towards "Normal" Yeast Cells

Yeast filtered from a "normal culture" and shaken for an hour in the rocker[2] with a 4% (by weight) solution of ethyl alcohol, behaves towards 0.005% methylene-blue as though distilled water had been used; the percentage of cells stained is only slightly increased. With 8% alcohol there is a notable increase in the number stained. Thus in phenol solutions containing 8% of alcohol the toxic effect of the phenol will

[1] Jour. Phys. Chem., 25, 1 (1921).
[2] Fraser: Loc. cit.

be supplemented by that of the alcohol, while in solutions containing 4% or less, the toxic effect of the alcohol as such may be neglected, and only its effect on the chemical potential of the phenol need be considered.

Chemical Equivalents

For the short range of dilute phenol solutions needed in the experiments with yeast, toluene is a more convenient immiscible solvent than kerosene, and the determinations were carried out as described by Lash Miller[1] in a thermostat at 25° C. In each case 19.90 cc of the aqueous or alcoholic solution of phenol was shaken with 5.01 cc of toluene, so that when equilibrium was reached about one-third of the phenol had gone into the upper layer. The concentration of phenol in the lower layer was determined by Lloyd's method,[2] a number of blanks having shown that as much as ten percent by weight of alcohol in the phenol solution does not interfere with the analysis. The following table gives the averages of a number of concordant determinations; when plotted they fall on three smooth curves, except for the two marked with an asterisk which have, therefore, been disregarded. Two determinations by L. M. fall within the range of my

0% Alcohol		3.75% Alcohol		7.50% Alcohol	
Aq. Layer	Tol. Layer	Aq. Layer	Tol. Layer	Aq. Layer	Tol. Layer
0.78	1.67	0.77	1.72	0.73	1.85
0.72	1.49	0.72	1.53	0.68	1.65
0.66	1.33	0.65	1.40[1]	0.64	1.45[1]
0.60	1.17	0.60	1.18	0.57	1.30
0.55	1.03	0.54	1.06	0.51	1.14
0.48	0.89	0.46	0.91	0.45	0.91
0.41	0.77				

The figures in the columns give the number of grams phenol in 100 cc of the lower and upper layer, respectively; 3.75% alcohol means 3.75 g ethyl alcohol in 100 cc of the lower layer.

[1] Jour. Phys. Chem., **24**, 564 (1920).

[2] Jour. Am. Chem. Soc., **27**, 16 (1905).

work; in both of them the upper layer was found to contain a little more phenol than given in my table.

From these determinations, by means of a graph, the following table of "toluene equivalents" was drawn up.

TOLUENE EQUIVALENTS

0% Alcohol	3.75% Alcohol	7.50% Alcohol
0.500	0.472	0.426
0.550	0.523	0.470
0.600	0.573	0.520
0.650	0.625	0.572
0.700	0.672	0.615
0.750	0.720	0.660

The figures in the same horizontal line give grams of phenol per 100 cc for three solutions, each containing the amount of alcohol stated at the head of its column, which are in equilibrium with the same solution of phenol in toluene.

Plating Equivalents

Yeast cells were obtained from a "normal" culture by filtration, using a small perforated plate and suction; they were washed on the filter paper twice with distilled water, suspended in distilled water, counted, and diluted so that when the suspension was added to 100 times its volume of the poisonous liquid in the "rocker" one cc of the poison would contain about 100 cells.[1] Immediately after adding the yeast to the poison, and at measured intervals thereafter, one cc of the mixture was removed, shaken with 10 cc melted wort-agar, and a plate poured.

In each of the two series three poisonous solutions were used, one free from alcohol and the other two containing 3.75% alcohol; the amounts of phenol in the two alcoholic solutions were so chosen that one contained a little less and the other a little more than enough to make them chemically equivalent to the alcohol-free solution. The table gives the percentage of cells "killed" by the three poisons acting at 25° C for the

[1] Details of the technique are given by Fraser: Jour. Phys. Chem., 25, 1 (1921).

number of minutes given under "min.;" these percentages are based on the number of colonies found on the plate poured immediately after adding the yeast—"100%" thus means no colonies on the plate. Under "M. B." is recorded the percentage of cells stained by 0.005% methylene-blue; they were taken from a fourth tube containing alcohol-free phenol solution and yeast to a count of about 15. The abbreviation "0—0.550" stands for "0% alcohol, 0.550% phenol."

0 — 0.550				3.75 — 0.500		3.75 — 0.520	
M. B.		Plates		Plates		Plates	
Min.	% Std.	Min.	% Kil'd	Min	% Kil'd	Min	% Kil'd
4	10	7	45	7	70	8	76
14	12	13	64	21	70	15	76
29	25	20	70	27	83	22	82
39	50	45	86	33	86	28	86
49	65	57	100	38	96	39	100
56	75			47	100		

The toluene equivalent of 0—0.550 is 3.75—0.523; it is evident that the "plating equivalent" contains much less phenol.

0 — 0.600				3.75 — 0.550		3.75 — 0.580	
M. B.		Plates		Plates		Plates	
Min.	% Std.	Min.	% Kil'd.	Min	% Kil'd	Min	% Kil'd.
5	5	5	1	15	56	8	100
10	15	15	56	21	60		
15	20	28	60	25	100		
20	28	40	88				
25	40						

The toluene equivalent of 0—0.600 is 3.75—0.573. In this case as in the last the "plating equivalent" would contain much less phenol; and my results with alcohol, like Fraser's with salt, show that chemically equivalent solutions are not

isotoxic towards yeast if inability to form colonies on wort-agar be taken as evidence of death.

Methylene-Blue Equivalents

As in the plating experiments, three solutions were placed in the rocker together; they were made up to twice the desired concentration and an equal volume of yeast suspension added; the count in the poison was about 15, corresponding to well under 0.1% by weight of yeast. Cells from a normal culture were used with the weaker poisons; with the stronger poisons older cells were used, so that the action of the poison might not be too rapid; but in every case the three solutions to be compared were seeded with the same suspension. Detailed figures for one series are given by way of illustration. In the table, the composition of the poison is given at the beginning of the second line, followed by the percentage of cells stained when an equal volume of 0.01% methylene-blue was added to one cc of the mixture, after the poison had acted on the cells for the number of minutes given in the first line.

A. Solutions Containing 3.75 Percent Alcohol

Time	4	5	8	11.5	14.5	18	22	26	29	32.5	35.5	38	39.5	min.
0—.500	30	37	40	50	55	60	65	70	86	90	92	94	100%	std.

Time	3	4.5	6.5	10	13	16.5	20.5	24	27.5	31.5	33.5	min.
3.75—.465	10	16	26	40	45	50	55	60	65	70	74%	std.
	36.5	39.5	42.5	44	45 min.							
	80	90	94	96	100% std.							

Time	2.5	4	6	8.5	12.5	15.5	19.5	23	26.5	30	min.
3.75—.475	16	33	60	65	75	80	90	93	95	100%	std.

The toluene equivalent of 0—0.500 is 3.75—0.472; the methylene-blue equivalent evidently lies between 3.75—0.465 and 3.75—0.475, say at 3.75—0.470.

Similar experiments were carried out with 0—0.550, 3.75—0.520 and 0.530; 0—0.600, 3.75—0.570 and 0.580; 0—0.650, 3.75—0.620 and 0.630; 0—0.700, 3.75—0.665 and 0.675; 0—0.750, 3.75—0.710 and 0.720. The figures obtained in each case were graphed, and the methylene-blue equivalent

determined. The results are given in the following table, toluene equivalents also being given for comparison.

METHYLENE-BLUE EQUIVALENTS

	3.75% Alcohol	
0% Alcohol	Tol. Equiv.	M. B. Equiv.
0.500% ph.	0.472% ph.	0.470% ph.
0.550	0.523	0.520
0.600	0.573	0.570
0.650	0.625	0.625
0.700	0.672	0.675
0.750	0.720	0.715

The above figures show conclusively that chemically equivalent solutions of phenol in water and in dilute alcohol are isotoxic towards yeast if the ability to stain with methylene-blue be taken as the criterion of death. In view of the number of manipulations involved in the toluene equilibrium experiments, and the number of burette readings in the volumetric estimation of phenol, it seems likely that the composition of chemical equivalents might be determined more accurately by the use of yeast and methylene-blue than by the "purely chemical" method. The M. B. equivalents certainly lie closer to a smooth curve than do these obtained with toluene.

B. Solutions Containing 7.50 Percent Alcohol

As already pointed out, it was only to be expected that phenol solutions containing 7.5% of alcohol would cause death in a shorter time than the equivalent solutions of phenol in water. This expectation was fully confirmed by three series of experiments carried out exactly like those with 3.75% alcohol, in which the following solutions were used: 0—0.550, 7.50—0.460 and 0.475; 0—0.600, 7.50—0.500 and 0.520; 0—0.650, 7.50—0.560 and 0.575. In every case the alcoholic solutions proved much the more toxic.

Summary

Yeast cells taken from a wort culture in which the alcohol produced by fermentation has reached a certain concentration,

are much more resistant to phenol than normal cells; addition of alcohol to the wort before seeding with yeast brings about the same effect in a shorter time. Conditions are specified under which yeast may be grown free from these abnormal ("resting") cells.

By analysis of liquids in equilibrium in the systems phenol-water-toluene, and phenol-alcohol-water-toluene, the chemical equivalents of solutions containing from 0.4% to 0.75% phenol and either 0%, 3.75% or 7.50% alcohol, have been determined.

If inability to grow colonies on wort-agar be taken as the criterion of death, solutions containing water, phenol, and 3.75% alcohol are more toxic than the chemically equivalent solutions without alcohol; but if ability to stain with methylene-blue be taken as the criterion, they are equally toxic. The M. B.-yeast method of obtaining the composition of chemically equivalent solutions is probably capable of greater accuracy than the purely chemical method.

Immersion in 8% solutions of alcohol in water increases the number of cells that stain with methylene-blue; consistently with this, solutions containing phenol, water, and 7.5% of alcohol increase the percentage of stained cells more rapidly than do chemically equivalent solutions of phenol in water.

The University of Toronto
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THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY FERRIC SALTS[1]

BY VAN L. BOHNSON

1. Historical

The decomposition of hydrogen peroxide, according to Thenard,[2] is either accelerated or retarded by nearly all substances. It is, therefore, an extremely useful reaction for studying the phenomena of catalysis in homogeneous systems, and is convenient for this purpose because of the readiness with which its progress may be quantitatively followed, and also because there are no disturbing substances formed, oxygen and water being the only products of the reaction. The action of various positive and negative catalysts on the decomposition of hydrogen peroxide has been exhaustively studied by various investigators, among them Bredig and his students,[3] who directed their attention to the accelerating effect of colloidal platinum and gold with various "poisoning" substances. Various enzymes,[4] such as haemase[5] and catalase,[6] have been shown to accelerate the decomposition; the action of a large variety of substances such as finely divided metals and metallic oxides, has been studied by Kastle and others.[7] There has, however, been little work done on the catalytic decomposition of hydrogen peroxide by salts of heavy metals. Schönbein studied the catalytic

[1] Part of a thesis submitted to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Thenard: Ann. Chim. Phys., (2) **9**, 96 (1818).

[3] Bredig and von Berneck: Zeit. phys. Chem., **31**, 296 (1901); Bredig and Ikeda: Ibid., **37**, 63 (1901); Bredig and Reinders: Ibid., **37**, 323 (1901).

[4] Schönbein: Zeit. f. Biol., (3) **140**, 325 (1867).

[5] Senter: Zeit. phys. Chem., **44**, 257 (1903).

[6] Loew: U. S. Dept. Agr. Report No. **68** (1901).

[7] Kastle and Clark: Am. Chem. Jour., **26**, 518 (1901); Loevenhart and Kastle: Ibid., **29**, 397 (1903).

effect of lead acetate,[1] and Porlezza and Norzi[2] the effect of manganese sulphate.

The influence of such salts on various oxidations by means of hydrogen peroxide has, however, been fairly extensively investigated. It has been found, for example, that ferrous sulphate accelerates the oxidation by hydrogen peroxide of glycol and glycerol,[3] tartaric acid,[4] certain hexoses,[5] and indigo.[6] The same salt increases the velocity of the reaction between hydrogen peroxide and hydriodic acid.[7] Sugars can be oxidized by hydrogen peroxide in the presence of ferric chloride,[8] and alcohols in the presence of manganous salts, the acetate being said to have the greater effect.[9]

Aside from its purely theoretical interest, the catalytic decomposition of hydrogen peroxide by iron salts is of great practical importance. Large quantities of it are manufactured for bleaching silk, feathers, hair, and ivory, and the solution must frequently extract from the tanks in which it is used or containers in which it is stored or shipped, traces of iron salts, which accelerate its decomposition. Even the glass containers in which it is kept in smaller quantities may contain a sufficient amount of iron to be effective; in fact, Tammann[10] expressed the opinion that a trace of iron oxide is the cause of the action of alkalis in decomposing the substance.

It has long been known that ferric chloride accelerates the decomposition of hydrogen peroxide in aqueous solutions;

[1] Schönbein: Jour. prakt. Chem., (1) **86**, 98 (1862).
[2] Porlezza and Norzi· Atti. Accad. Lincei, **22** I, 238 (1869).
[3] Fenton and Jackson: Jour. Chem. Soc., **75**, 4 (1899).
[4] Fenton: Ibid., **65**, 899 (1894); Fenton and Jones: Ibid., **77**, 69 (1900).
[5] Cross, Bevan and Smith: Proc. Chem. Soc., **14**, 115 (1898).
[6] Schönbein: Jour. prakt. Chem., **75**, 79 (1858); **78**, 90 (1859).
[7] Schönbein: Ibid., **79**, 66 (1859); Brode: Zeit. phys. Chem., **37**, 257 (1901).
[8] Fischer and Busch: Ber. deutsch. chem. Ges., **24**, 1871 (1891).
[9] Chauvin: Ann. fals., **6**, 463; Jour. Chem. Soc., **104**, 1037 (1913).
[10] Tammann: Zeit. phys. Chem., **4**, 441 (1889).

Tammann[1] noted that it is a more active catalyst than the alkalis. Spring[2] describes the action as follows:

"If to a dilute solution of ferric chloride, of which the color is a clear yellow, there is added a solution of hydrogen peroxide, the color deepens immediately and takes on the brown tint of the basic chloride; the evolution of oxygen then begins and is accelerated with rise of temperature." Spring believes that the decomposition of the hydrogen peroxide is in part due to the formation of colloidal ferric hydroxide or a colloidal basic salt. He also believes that there is a chemical reaction between the hydrogen peroxide and the ferric chloride.

Bredig and von Berneck[3] disagree with Spring's views, and give experimental evidence to show that colloidal ferric hydroxide has almost no action on hydrogen peroxide solutions, and that iron salts (as typified by ferrous sulphate) are most active in nearly neutral solutions. This activity they admit may be due to the formation of a basic salt or to the formation of a peroxidized compound of iron.

It is the purpose of this investigation to study the relative effects of different ferric salts upon the decomposition of hydrogen peroxide, both alone and in the presence of additional substances, with the purpose of arriving at a better understanding of the mechanism of the reaction.

2. Preliminary Experiments—Evidence of an Intermediate Compound

If a solution of a ferric salt (the chloride, nitrate, or sulphate) is diluted so as to be nearly colorless, and to 10 cc of the solution a drop or two of 30% hydrogen peroxide is added, a fairly deep coloration results, which in this dilution has a distinct lavender tint. The solution begins at once to evolve oxygen, and when the evolution of gas ceases has again become practically colorless; quantitative experiments show the hydrogen peroxide to be completely decomposed. Such

[1] Tammann: Ziet. phys. Chem., 4, 441 (1889).

[2] Spring: Bull. Acad. roy. Belg., III, 30, 48 (1895).

[3] Bredig and von Berneck: Loc. cit.

behavior indicates the probability of the formation of an intermediate compound, which is by no means the basic salt assumed by Spring.[1]

The theory which explains certain catalytic phenomena by assuming the formation of an intermediate compound is not new, having been first promulgated by Desormes and Clement[2] in connection with the action of nitric oxide on the oxidation of sulphur dioxide. Bredig and Weinmayr,[3] who studied the periodic decomposition of hydrogen peroxide in contact with metallic mercury, believe it to be due to the alternate formation and decomposition of a peroxide of mercury, which has been isolated by Antropoff[4] and found to be a dark red, extremely unstable substance. Job[5] and Baur[6] explain the oxidizing action of hydrogen peroxide in the presence of cerium salts as due to the intermediate formation of cerium peroxide, a compound which has also been isolated.[7] Brode[8] explains the accelerating action of molybdic acid on the reaction between hydrogen peroxide and hydriodic acid by assuming the intermediate formation of permolybdic acid.[9] The oxidation of sodium thiosulphate by hydrogen peroxide in the presence of the same catalyst is explained in the same manner.[10] Schönbein[11] thought the action of lead acetate on hydrogen peroxide to be due to the alternate oxidation of lead oxide and reduction of the peroxide.

There are a large number of compounds of relatively high oxidation known to be formed by means of hydrogen

[1] Spring: Loc. cit.

[2] Desormes and Clement: Annales de Chimie, **59**, 329 (1806).

[3] Bredig and Weinmayr: Zeit. phys. Chem., **42**, 601 (1903).

[4] Antropoff: Jour. prakt. Chem., **77**, 273 (1908).

[5] Job: Comptes rendus, **134**, 1052 (1902).

[6] Baur: Zeit. anorg. Chem., **30**, 250 (1902).

[7] Cleve: Bull. Soc. chim. Paris, **43**, 53 (1885); see also Hermann: Jour. prakt. Chem., **30**, 184 (1843); Mengel: Zeit. anorg. Chem., **19**, 71 (1899).

[8] Brode: Zeit. phys. Chem., **37**, 257 (1901).

[9] Berwald: Ber. deutsch. chem. Ges., **18**, 1206 (1885).

[10] Abel and Baum: Monatshefte, **34**, 425.

[11] Schönbein: Loc. cit.; see also Zotier: Bull. Soc. chim. Paris, **15**, 402 (1871).

peroxide, among them perchromic acid,[1] peruranic acid,[2] titanium peroxide,[3] zinc peroxide,[4] bismuth peroxide,[5] and various peroxidized compounds of iron.[6]

The distinct lavender color obtained when hydrogen peroxide reacts on dilute ferric salt solutions indicates a possibility that ferric acid is the intermediate compound formed in the reaction. The acid itself, owing to its instability, has never been isolated, but some of its salts are well known,[7] and in dilute solution have the characteristic lavender color mentioned. Attempts were made to isolate the colored intermediate product by shaking out with an immiscible solvent, but it proved to be insoluble in all the solvents used such as ether, chloroform, carbon tetrachloride, benzene, etc., neither could it be precipitated out by cooling an alcohol solution in freezing mixtures. Since dilute ferric chloride solutions must be used in order to avoid violent decomposition of the hydrogen peroxide, the amount of intermediate compound formed is consequently very small and is apparently quite soluble in water. "It must be admitted even by opponents of the theory that the intermediate compound must be labile or unstable for the catalyst to exert a great activity."[8]

If an excess of alkali is added to the mixture of hydrogen peroxide and ferric salt solution before the former has had time to decompose, a very deep red precipitate is obtained, which after thorough washing yields a small amount of oxygen upon ignition. Manchot[9] claims to have obtained a superoxide Fe_2O_5, which may possibly have been a mixture of a compound of even higher oxidation with Fe_2O_3.

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[1] Moissan: Comptes rendus, **97**, 96 (1883).

[2] Fairley: Jour. Chem. Soc., **31**, 127 (1877).

[3] Schöne: Dingler's Pol. Jour., **210**, 317 (1873); see also Classen: Ber. deutsch. chem. Ges., **21**, 370 (1888).

[4] Ebler and Krause: Zeit. anorg. Chem., **71**, 150 (1911).

[5] Hanus and Kallauner: Ibid., **70**, 232 (1911).

[6] Manchot and Wilhelms: Liebig's Ann., **325**, 105 (1902); Ber. deutsch. chem. Ges., **34**, 2479 (1901); Pellini and Meneghini: Zeit. anorg. Chem., **62**, 203 (1909).

[7] Rosell: Jour. Am. Chem. Soc., **17**, 760 (1895). A review.

[8] Rideal and Taylor: "Catalysis in Theory and Practice," p. 39.

[9] Manchot: Loc. cit.

When an excess of a cold mixture of potassium hydroxide and "perhydrol" is added to a ferric chloride solution a solution is obtained having a deep red color. If barium hydroxide is now added to this solution a deep claret-red gelatinous precipitate is obtained. This precipitate when washed dissolves in hydrochloric acid with the liberation of chlorine, indicating it to be the barium salt of a higher oxide of iron mixed no doubt with considerable ferric hydroxide. Barium ferrate as ordinarily prepared is not gelatinous but resembles barium sulphate and barium chromate in its physical state. However, barium sulphate is also known to exist under certain conditions in a gelatinous form and barium chromate was produced in the course of this research in the form of a gelatinous precipitate as follows:

Chromium chloride solution when warmed to about 40° accelerates the decomposition of hydrogen peroxide. The solution changes from green to yellow indicating the formation of the chromate ion and back to the green color of the chromic salt at the end of the reaction. When barium hydroxide was added to the solution at its yellow stage a flocculent yellow precipitate was obtained which was found to be a mixture of barium chromate and chromium hydroxide.

3. Mechanism of the Reaction

Preliminary Discussion.—The results of the qualitative experiments above described indicate that there is formed in the reaction between hydrogen peroxide and ferric salts an intermediate product of higher oxidation, probably the unstable ferric acid. From the composition of its derivatives the formula of this acid may be assumed to be H_2FeO_4. With this assumption the general reaction for any ferric salt may be formulated then as follows, R indicating any monovalent acid radical.

$$(1) \quad 2FeR_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 6HR$$

To account for the liberation of oxygen in the reaction there are now two possibilities:

(*a*) Simple decomposition of the ferric acid according to the equation

$$2H_2FeO_4 \longrightarrow Fe_2O_3 + 2H_2O + 3O, \text{ or}$$

(*b*) Reduction of the ferric acid by hydrogen peroxide thus:

$$2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2$$

with subsequent solution in both cases of the hydrated ferric oxide in the acid resulting in equation (1); such a reaction is similar to the reduction of potassium permanganate by hydrogen peroxide in acid solution.

If (*a*) is the case it might be expected that in the presence of hydrochloric acid the latter would be oxidized to liberate chlorine; in fact barium ferrate dissolves in hydrochloric acid with immediate evolution of chlorine. However, no chlorine was detected among the products of the reaction between ferric chloride and hydrogen peroxide. These results seem to dispose of the first assumption leaving the second to be confirmed.

With this end in view barium ferrate was prepared by precipitating an alkaline potassium ferrate solution with barium chloride. The potassium ferrate was prepared by passing a rapid stream of chlorine into a suspension of ferric hydroxide in concentrated potassium hydroxide.[1] The precipitated barium ferrate was washed with distilled water until shown to be free from alkali and hypochlorites. It was then dissolved in dilute acetic acid, with which it forms a fairly stable deep red solution although with the strong mineral acids it immediately decomposes, forming the corresponding ferric salt.

To the acetic acid solution, which upon examination proved to be evolving a gas only very, very slowly, a little hydrogen peroxide was added. Oxygen was at once copiously evolved and in the course of a few minutes the solution had become the color of the dilute ferric acetate solution. This

[1] Merz: Jour. prakt. Chem., 101, 268 (1867).

indicates that ferric acid in acid solution is reduced by hydrogen peroxide as follows:

$$2H_2FeO_4 + 3H_2O_2 + 6HR \longrightarrow 2FeR_3 + 8H_2O + 3O_2$$

For the sake of simplicity we may assume this to be taking place in the following successive stages:

$$2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2$$
$$2Fe(OH)_3 + 6HR \rightleftarrows 2FeR_3 + 6H_2O$$

an assumption which is supported by the fact that the alkali salts of ferric acid decompose in dilute neutral solution, precipitating ferric hydroxide.

Summarizing the discussion of the last few pages we may assume the catalytic decomposition of hydrogen peroxide by ferric salts in general to take place in the following successive stages:

$$(1)\quad 2FeR_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 6HR$$
$$(2)\quad 2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2$$
$$(3)\quad 2Fe(OH)_3 + 6HR \rightleftarrows 2FeR_3 + 6H_2O$$

Thus the complete reaction may be expressed by the simple equation

$$6H_2O_2(+2FeR_3) \longrightarrow 3O_2 + 6H_2O(+2FeR_3)$$

In the above series of equations (2), representing the reaction in which a gas is evolved, is the one actually measured by the gasometric method used in this research. Reaction (1) is apparently instantaneous and reaction (3) has only an indirect effect on the evolution of oxygen.

4. A Quantitative Study of the Reaction

Method.—For measuring the rate of evolution of oxygen, the gasometric method described in the preceding paper was used. It was there shown to be capable of giving very accurate results. All experiments were carried on at 25°.

Materials.—The hydrogen peroxide and water were the same as used in the experiments described in the preceding paper. The salts used as catalysts were recrystallized several times from specially distilled water. The ferric salts were shown to be free from manganese compounds and concentrated stock solutions were made up of which the iron content

was determined by titration with potassium dichromate. Catalyst solutions of the desired concentration were prepared immediately before use (in order to minimize the effect of hydrolysis) by diluting the stock solutions.

Results—Explanation of Tables.—The tables of data representing the velocity of evolution of oxygen in the presence of various substances have been condensed as in the preceding paper and summarized in separate tables. The following symbols are used:

t the time in minutes.

x milligrams of oxygen evolved in the time t.

a total weight (in milligrams) of oxygen evolved.

K_r $10^4 \times 0.4343$ K (for first order reaction).

C Concentration in mols per liter.

The velocity constants were calculated as described in the preceding paper; in summarizing them the *first* constant of any series is selected for reasons expressed in section 7b as most closely approximating the true specific velocity. Concentrations are expressed in mols per liter except in the summaries where for the purpose of comparison they are expressed in gram equivalents per liter.

It should be noted that the velocities obtained in these experiments so far exceed that of the spontaneous decomposition of the hydrogen peroxide at 25° that the effect of the latter may be ignored.

5. Factors in the Velocity of the Reaction

In the cycle of reactions:

(1) $2FeR_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 6HR$
(2) $2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2$
(3) $2Fe(OH)_3 + 6HR \rightleftarrows 2FeR_3 + 6H_2O$

the equilibrium of reaction (1) depends upon the following:

(*a*) The concentration of ferric salt. This depends not only upon the amount originally present but also upon the rate with which it is renewed by reaction (3).

(*b*) The ionization of the ferric salt.

(*c*) The concentration of hydrogen peroxide. In all experiments an initial concentration of about 0.12 mol per

liter was used which is greatly in excess of the concentration of catalyst.

(*d*) The water present, which is in large excess, as experiments are conducted in dilute solutions. Its concentration may be taken as unity.

(*e*) The concentration of the ferric acid which is probably but little ionized.

(*f*) The hydrogen ion concentration.

(*g*) The nature and concentration of the anions.

Reaction (2) in which the oxygen is evolved is the relatively slow irreversible reaction whose velocity is measured. It is known that high pressures of oxygen have no effect on the rate of decomposition of hydrogen peroxide.[1] The initial velocity of this reaction will depend upon:

(*a*) The concentration of hydrogen peroxide.

(*b*) The concentration of ferric acid which is dependent upon the equilibrium in reaction (1).

The rate of solution of ferric hydroxide in the acid present, according to reaction (3), will, if the physical condition of the ferric hydroxide is always the same, be also dependent upon the hydrogen ion concentration. It is thus apparent that increase in the hydrogen ion concentration will have two separate opposing effects, the one shifting the equilibrium so as to produce less ferric acid, the other increasing the rate at which the catalyst is renewed, thus tending to produce more ferric acid. In any such cycle of mutually interdependent reactions the same sort of influence of one of the products of the first reaction should be expected. The actual total influence of change in hydrogen ion concentration, then, depends upon the relative magnitudes of the two opposing effects.

The equilibrium of reaction (3) is also a factor in the system, that is, the extent to which the ferric hydroxide is again converted into active catalyst.

In order to investigate the actual results of altering the several variables the influence of the following variables on the reaction was studied.

[1] Spear: Jour. Am. Chem. Soc., 30, 195 (1908).

(1) The concentration of different ferric salts.

(2) Excess of free acid.

(3) The effect of salts having an ion in common with the catalyst.

(4) The effect of sodium salts of different acids.

(5) The joint effect of mixed catalysts.

(6) The effect of solvents such as were used in the investigation reported in the preceding paper.

6. The Order of the Reaction

Hydrogen peroxide in its decomposition usually conforms to the mathematical expression for a monomolecular reaction. Such is the case, for example, when it is catalyzed by colloidal gold [1] colloidal platinum [2] or the iodide ion.[3] On the other hand it has been found to follow the second order of reaction[4] when decomposed in quinoline solution under the catalytic influence of manganese acetate.

The equation

$$2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2$$

of which the velocity is measured is that of a quinquemolecular reaction. Such reactions as measured by our present methods are extremely rare however and it should therefore be of interest to determine the actual order which this reaction follows. In the following table K_1 represents the velocity constant calculated according to the expression for a first order reaction, and K_2 that for a second order reaction.

TABLE I—ORDER OF THE REACTION
$FeCl_3$ = 0.002974 mol per liter. a = 44.59

t	x	K_1	K_2
2	6.83	0.0361	0.002028
5	14.75	0.0349	0.002217
8	21.09	0.0347	0.002516
14	29.78	0.0341	0.003222
21	35.65	0.0332	0.004259

[1] Bredig and von Berneck, Bredig and Ikeda: Loc. cit.

[2] Bredig and Reinders: Loc. cit.

[3] Walton: Zeit. phys. Chem., **47**, 185 (1904).

[4] Walton and Jones: Jour. Am. Chem. Soc., **38**, 1956 (1916).

An examination of the constants obtained will show that the reaction is not of the second order, while the constants for the first order agree relatively closely. There is obviously, however, a slight disturbing effect due to a side reaction which will be discussed later, which evidences itself in the decrease in the value of the constants in the first column.

The reaction measured, notwithstanding the form of its equation, is apparently one of the first order. This result may be explained by the fact that the initial concentration of the hydrogen peroxide present (approximately 0.12 mol per liter) is greatly in excess of that of the iron compound (the ferric chloride being present in a concentration of 0.002974 mol per liter). Since the concentration of the intermediate product (the effect of hydrolysis excepted) remains constant throughout any given experiment, the velocity will vary only as the concentration of hydrogen peroxide varies, thus fulfilling the requirements for the velocity of a monomolecular reaction. In two different experiments, other conditions being constant, the relative velocities of decomposition of the hydrogen peroxide will depend upon the relative concentration of the catalyst.

7a. Effect of Concentration of the Catalyst

Most frequently in the case of a monomolecular reaction, if there are no disturbing effects, the velocity of the reaction is proportional to the concentration of catalyst present. For example, the speed of inversion of cane sugar in dilute acid solutions,[1] and the rate of decomposition of diazo acetic ester,[2] are proportional to the concentration of hydrogen ion present; the velocity of condensation of acetone is proportional to the hydroxyl ion concentration,[3] while that of the synthesis of benzoin is proportional to the concentration of cyanide ions.[4] On the other hand, certain investigators have shown the ve-

[1] Ostwald: Jour. prakt. Chem., **28**, 449 (1883); Trevor: Zeit. phys. Chem., **10**, 330 (1892); Palmaer: Ibid. **22**, 504 (1897).

[2] Fraenkel: Zeit. phys. Chem., **60**, 202 (1907).

[3] Koelichen: Zeit. phys. Chem., **33**, 129 (1900).

[4] Stern: Zeit. phys. Chem., **50**, 513 (1905).

locities of the following reactions to be proportional to the square of the concentration of the catalyst: the oxidation of hydriodic acid by bromic acid[1] and by iodic acid [2] and the chlorination of benzene.[3] The dissolution of arsenious oxide is accelerated by both hydrogen and hydroxyl ions and the rate is proportional to the square root of the concentration of these ions.[4]

The effect of the concentration of the ferric salts used as catalysts is shown in Tables II, III, IV, and V and graphically illustrated in Fig. 1. In Table V, the "mean K_1" is the mean value of two or more first constants in separate experiments. As heretofore mentioned the first constant is selected as more nearly approximating the true value.

The identical effect of equivalent quantities of ferric chloride and ferric nitrate is striking. The lower half of the curve for these two substances shows that the velocity of decomposition of hydrogen peroxide is directly proportional to the concentration of the ferric salt when the latter is present in not more than 0.002 mol per liter. The slight sagging of the curve near the origin, which indicates a lower velocity than that expected, may be due to the fact that hydrolysis of the catalyst in this concentration would remove a larger proportion of it from the sphere of chemical action. In like manner, hydrolysis of the ferric salt in greater concentrations may produce proportionately larger quantities of free acid which, as will be shown, retard the reaction. This effect would then account for the deviation of the curve from the proportionality line in concentrations above the 0.002 mol per liter. Another influence which is doubtless at work is the decreased ionization of the ferric salts in larger concentrations with a consequent displacement of the equilibrium

$$2FeCl_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 6HCl$$

[1] Magnanini: Gazz. chim. ital., **20**, 390 (1890).
[2] Dushman: Jour. Phys. Chem., **8**, 453 (1904).
[3] Slator· Zeit. phys. Chem., **45**, 513 (1903).
[4] Drucker: Zeit. phys. Chem., **36**, 693 (1901).

TABLE II

Ferric Chloride as a Catalyst

C = mols $FeCl_3$ per liter

t	x	K_s	t	x	K_s	t	x	K_s
1. C=	.000297		2. C=	.000297		3. C=	.000595	
a=	45.73		a=	45.47		a=	42.35	
20	5.38	27.2	20	4.80	24.2	12	6.39	59.2
76	14.62	22.0	76	11.19	16.1	30	12.82	52.2
239	24.93	14.3	239	14.55	7.0	76	21.75	41.2
						239	34.28	30.1
4. C=	.000595		5. C=	.001487		6. C=	.001487	
a=	43.10		a=	42.58		a=	42.00	
12	4.93	44.0	3	5.74	209	4	7.69	219
30	9.80	37.3	6	10.55	206	8	13.63	213
76	16.05	26.6	10	15.90	203	13	19.22	204
239	20.61	11.8	16	21.97	197	18	23.45	197
			27	29.24	186	28	29.09	183
			38	33.47	176	41	33.35	167
7. C=	.001487		8. C=	.002082		9. C=	.002082	
a=	39.53		a=	37.24		a=	38.94	
4	6.78	204	4	8.06	265	4	8.60	271
8	12.00	193	8	14.31	263	8	15.18	268
13	16.97	187	13	20.04	258	13	21.19	262
18	20.72	179	18	24.06	251	18	25.36	254
28	25.88	165	28	28.96	233	28	30.65	240
41	29.68	147						
10. C=	.002974		11. C=	.002974		12. C=	.002974	
a=	39.55		a=	48.41		a=	44.59	
3	8.94	371	4	13.59	358	2	6.83	361
6	15.79	369	8	23.16	353	5	14.75	349
9	21.10	368	12	30.07	351	8	21.09	347
13	26.16	362	17	35.94	347	14	29.78	341
16	29.06	360	22	39.73	340	21	35.65	332
13. C=	.004864		14. C=	.004864				
a=	41.26		a=	43.85				
2	8.24	484	3	12.30	476			
5	17.27	471	6.5	22.36	476			
9	25.20	455	9	27.45	474			
14	31.13	435	13	33.13	470			

TABLE III

Ferric Nitrate as a Catalyst

C = mols $Fe(NO_3)_3$ per liter

t	x	K_s	t	x	K_s	t	x	K_s
1. C=	.000187		2. C=	.000748		3. C=	.000935	
a=	49.16		a=	43.82		a=	44.63	
22	1.15	4.7	9	6.21	73.7	6	6.58	115
60	2.56	3.9	19	10.85	65.0	13	12.43	109
			32	14.98	56.7	24	18.86	99.4
			55	19.78	47.4	39	24.68	89.7
						59	29.62	80.2
4. C=	.001122		5. C=	.001495		6. C=	.001869	
a=	43.35		a=	41.50		a=	41.68	
4	5.20	138	4	6.88	197	4	8.52	248
13	13.94	129	9	13.66	192	8	15.25	247
22	19.72	120	15	19.79	188	14	22.63	243
30	23.45	113	24	26.11	179	21	28.44	237
45	28.33	103	41	32.53	162	34	34.42	223
7. C=	.00243		8. C=	.002803		9. C=	.003177	
a=	42.16		a=	44.55		a=	43.66	
4	10.14	298	4	11.64	329	4	12.43	364
8	17.77	297	7	18.16	325	8	21.11	359
13	24.56	291	12	26.02	317	12	27.06	367
22	32.00	281	19	32.9	307	20	34.36	335
10. C=	.003738		11. C=	.004672				
a=	43.21		a=	45.07				
4	13.35	401	3	12.53	472			
8	22.43	397	7	23.75	464			
13	29.81	391	12	32.2	454			
20	35.59	377	19	38.19	430			

to the left reducing the concentration of ferric acid and on that account retarding the evolution of oxygen.

The marked differences between the velocities due to equivalent amounts of the nitrate and chloride on the one hand and the sulphate on the other demand further consideration. Since all salts with few exceptions, are quite highly ionized, no such difference in the ionization of ferric chloride and ferric sulphate can be assumed as to account for the great

Table IV

Ferric Sulphate as a Catalyst
C = mols $Fe_2(SO_4)_3$ per liter

t	x	K_s	t	x	K_s	t	x	K_s
1. C=	.00048		2. C=	00048		3. C=	.00096	
$a=$	46.82		$a=$	43.70		$a=$	43.18	
12	6.76	56.4	9	5.34	62.9	10	8.49	95.1
24	11.80	52.6	24	11.14	53.2	21	15.71	93.5
40	16.98	48.2	40	16.22	50.3	34	21.87	90.2
61	22.12	45.5	64	21.84	47.0	51	27.67	87.2
83	26.04	42.5				71	32.30	84.3
4. C=	.001923		5. C=	.001923		6. C=	.002403	
$a=$	47.25		$a=$	44.67		$a=$	41.78	
5	6.05	119	6	7 02	124	7	8.06	132
12	12.85	115	12	12.76	122	14	14.42	131
21	19.89	113	30	25.00	118	23	20.86	130
31	25.87	111	47	32.03	116	36	27.39	130
50	33.58	108				50	32 23	128
7. C=	.003365		8. C=	.004807		9. C=	.006056	
$a=$	43.16		$a=$	41.42		$a=$	42.20	
8	10.19	146	6	8.36	163	4	5.97	166
15	16.83	143	13	15.72	160	12	15.26	162
23	22.74	141	21	22.09	158	23	23.91	157
36	29.45	139	34	29.05	158	33	29 25	156
51	34.38	136	49	33 92	152			
0. C=	.00961		11. C=	.00961		12. C=	.01923	
$a=$	45.38		$a=$	45.08		$a=$	47.51	
6	9.91	178	5	8.42	179	5	9.83	201
11	16.16	174	10	15.08	177	10	17.30	196
16	21.36	172	17	22.17	173	16	24.03	191
22	26.35	171	24	27.45	170	24	30.52	186
30	31.25	169	34	32.86	166	34	35.88	180
3. C=	.01923							
$a=$	43.41							
4	7.84	216						
9	15.22	208						
14	20.93	204						
20	26.13	200						
28	31.17	196						

TABLE V

Summary: Effect of Concentration of Catalyst

Ferric Chloride		Ferric Nitrate		Ferric Sulphate	
Equivalents per Liter	Mean K_s	Equivalents per Liter	Mean K_s	Equivalents per Liter	Mean K_s
0.000297	25.7	0.000187	4.7	0.00096	59.6
0.000595	51.6	0 000748	73.7	0.00192	95.1
0.001487	211	0.000935	115	0.003846	122
0.002082	268	0.001122	138	0.004806	132
0 002974	363	0 001495	197	0.00673	146
0 004864	480	0 001869	248	0 009614	163
		0 00243	298	0.01211	166
		0.002803	329	0 01922	178
		0.003177	364	0.03846	208
		0 003738	401		
		0 004672	472		

difference in their relative effects. It is therefore obvious that in the two equilibria:

$$(a_1)\quad 2FeCl_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 6HCl$$
$$(b_1)\quad Fe_2(SO_4)_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 3H_2SO_4$$

the chief differences lie: (1) in the strength of the acids formed in the reactions, that is, in the hydrogen ion concentration existing when equilibrium has been attained, and (2) in the different kinds of ions present, namely the chloride ion in the one case and the sulphate ion in the other.

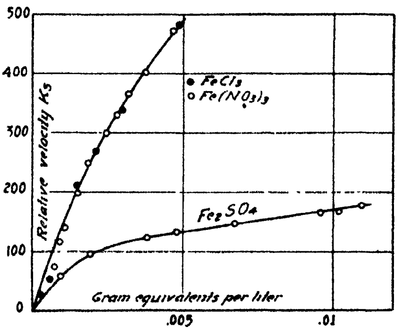

Fig. 1

Effect of Concentration of Catalyst

A discussion of this effect is intimately related to the effects of different acids and their salts upon ferric salt catalysis and will be reserved until these effects have been shown.

It is worthy of note that ferric salts accelerate the decomposition of hydrogen peroxide much more than does an

equivalent amount of sodium iodide as is graphically shown in Fig. 1. The curve for this substance is plotted from data obtained in the preceding paper which agree closely with the values obtained by Walton.[1]

7b. Effect of Hydrolysis of the Catalyst

It has already been noted that the value for the specific velocity as calculated by using the expression for a monomolecular reaction decreases slightly as the reaction proceeds and it has been suggested that this decrease is due to a simultaneous side reaction. Reference to Tables II, III, and IV, reveals that this decrease is relatively greater in more dilute solutions of the catalyst.

According to the method used in determining the reaction velocity one cubic centimeter of a ferric salt (catalyst) solution is suddenly diluted to twenty-six times its volume at the outset of the reaction. It is well known that iron salts, being salts of a weak base are readily hydrolyzed, and it is apparent that hydrolysis must at once set in with the resultant formation of ferric hydroxide or basic salts of variable composition. Spring[2] as already noted believes the decomposition of the hydrogen peroxide to be in some way connected with this hydrolysis, but it seems possible on the contrary that the hydrolysis may be more intimately connected with the decrease in the velocity constant. To verify the belief that such is the case the following series of experiments was carried out.

(1) A ferric chloride solution which had been in use as a catalyst when freshly prepared had after standing for a month become opalescent, indicating that considerable hydrolysis had taken place. No actual precipitation had yet taken place so that presumably a homogeneous sample was obtained. When used as a catalyst it gave considerably lower results than it had when freshly prepared:

[1] Walton; Loc. cit.
[2] Spring: Loc. cit.

1. Freshly prepared — 2. Partially hydrolyzed

t	x	K_s	t	x	K_s
a =	39.55		a =	43.51	
3	8.94	371	5	13.56	324
6	15.79	369	9	21.30	324
16	29.06	360	31	38.50	303

The sudden dilution of the solution at the outset of the reaction would cause further hydrolysis, with a consequent lowering in value for the later constants of the series.

(2) Since colloidal ferric hydroxide may be one of the products of hydrolysis its effect on the decomposition of hydrogen peroxide is of interest. Bredig and von Berneck[1] showed its accelerating action to be negligible. Their results were confirmed. A colloidal ferric hydroxide sol which had been dialyzed 26 days with tap water and 5 days with distilled water was used as a catalyst, the reaction flask containing 0.0116 mol per liter of $Fe(OH)_3$; in 60 minutes only 2.35 mg of oxygen were evolved from a solution containing 150 mg of hydrogen peroxide.

(3) It was also shown that the basic salt formed by the hydrolysis of ferric chloride has but little effect. The precipitate which had formed in a dilute solution of the salt after long standing was filtered and thoroughly washed. Several grams of this material in the reaction flask caused an evolution of only 3.69 mg of oxygen in 60 minutes. The effect of this substance is, therefore, negligible.

(4) According to the usual method of procedure in the experiments the catalyst solution is greatly diluted just at the outset of the reaction. It was desired to find out if lower constants would be obtained if the catalyst were allowed to hydrolyze for a time before coming in contact with the hydrogen peroxide. For this purpose two parallel experiments were carried on with a catalyst solution of the same concentration. In Experiment I, the catalyst was added in the

[1] Bredig and von Berneck: Loc. cit.

usual manner, being dropped into the hydrogen peroxide solution at the beginning of the determination. In Experiment II an equal amount of the catalyst was diluted to 25 cc and allowed to stand several hours. The hydrogen peroxide was then added at the beginning of the determination. The following results were obtained:

I. No Previous Hydrolysis II. Previous Hydrolysis

t	x	K_s	t	x	K_s
a =	41.16		a =	44.40	
3	7.28	282	2	4 99	259
6	13.32	283	6	13.17	255
10	19.58	280	10	19.65	254
17	27.28	277	17	27.65	249
29	34.17	259	29	35.21	236

These results further indicate that ferric chloride which has been allowed to hydrolyze does not have as great an accelerating effect as the salt which has not hydrolyzed to so great an extent. It will be noted also that the total relative decrease of the constant in Experiment II is less than that in Experiment I, indicating that the rate of hydrolysis in the former is slower. The fact that the constants decrease at all indicates that the hydrolysis had not yet reached an equilibrium.

The preceding series of experiments serves to show that hydrolysis of the catalyst decreases the catalytic effect; it removes active catalyst from the sphere of action by producing an insoluble inactive substance. At the same time it produces free acid in the solution which has a further retarding effect, as will be shown.

It is now evident that in any experiment the first constant of the series, obtained before the effect of hydrolysis has become marked, more closely approximates the true specific velocity. It must be admitted that even the constant thus selected is smaller than the actual value owing to some hydrolysis which may already have taken place in the standard catalyst solution. Thus the constants obtained are

relative and not absolute values for the catalysis by iron salts. It is therefore the first constant in each case which has been included in the summary tables and plotted in the various curves.

7c. Effect of Hydrogen Ion Concentration

The general statement is often made that acids preserve hydrogen peroxide.[1] Thenard[2] has shown that the presence of free acids retards the catalytic action of colloidal gold; Walton and Judd[3] found sulphuric acid to be an efficient preservative. Schönbein[4] reports that acids decrease the velocity of oxidation of hydriodic acid by hydrogen peroxide; Brode[5] reports acetic and oxalic acids to be especially effective on this reaction. Porlezza and Norzi[6] found that uric, benzoic, oxalic and hippuric acids retard the catalytic action of manganese sulphate.

Qualitative experiments showed that a few drops of hydrochloric acid in the ferric chloride solution materially retard the rate of evolution of oxygen and at the same time prevent the appearance of the violet color of the ferric acid; if the acid is added during the reaction the color is at once discharged and the evolution of gas practically ceases.

The effect of addition of acid upon the equilibrium:

$$2FeCl_3 + 3H_2O_2 + 2H_2O \rightleftharpoons 2H_2FeO_4 + 6HCl$$

was investigated colorimetrically. A series of Nessler tubes containing equal volumes of solution having the same amount of ferric chloride but varying amounts of $N/100$ hydrochloric acid were examined and it was found that the color was lighter, the more acid there was present. It is therefore clear that free acid, as would be expected displaces the above equilibrium to the left.

The data given in Tables VI VII and VIII show the effect of different concentrations of acid upon the velocity of de-

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[1] Spring: Zeit. phys. Chem., **19**, 161 (1896).

[2] Thenard: Ann. Chim Phys., (2) **9**, 96 (1818).

[3] Walton and Judd: Zeit. phys. Chem , **83**, 315 (1913).

[4] Schönbein: Loc. cit.

[5] Brode: Loc. cit.

[6] Porlezza and Norzi: Loc. cit.

composition of hydrogen peroxide when catalyzed by ferric chloride; those in Table IX show the effect of sulphuric acid upon the ferric sulphate catalysis. The results are shown graphically in Figs. 2, 3 and 4, and indicate that hydrogen

TABLE VI

The Effect of Hydrochloric Acid on the Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter

C = mols per liter of HCl

t	x	K_s	t	x	K_s	t	x	K_s
1. C=	.000425		2. C=	.000850		3. C=	.001275	
a=	46.99		a=	43.78		a=	40.98	
4	11.97	319	4	10.56	299	4	9.32	280
8	20.68	315	8	18.52	298	8	16.55	281
13	28.46	311	13	25.85	298	13	23.31	281
17	32.91	308	17	30.07	297	17	27.23	279
23	37.39	300	24	35.20	295	24	31.98	274
4. C=	.002125		5. C=	.00340		6. C=	.00425	
a=	26.58		a=	45.47		a=	40.04	
5	6.95	263	6	10.96	200	3	4.61	177
11	12.76	258	10	16.93	202	7	9.99	178
16	16.16	255	15	23.07	205	12	15.63	179
19	17.74	252	25	31.68	207	22	24.14	182
			32	35.54	206	29	28.28	183
7. C=	.00538		8. C=	.008608		9. C=	.01291	
a=	45.24		a=	47.49		a=	43.75	
5	7.02	146	8	7.69	95.9	10	6.53	70.2
11	14.15	148	15	13.71	98.6	20	12.41	72.4
19	21.87	151	23	19.80	102	36	20.32	75.3
29	29.05	153	36	27.45	104	56	27.80	77.0
44	35.91	155	53	34.46	105			
10. C=	.01722		11. C=	.01937		12. C=	.02152	
a=	46.10		a=	47.44		a=	45.74	
12	6.10	51.4	15	6.40	42.0	17	6.70	40.5
25	12.02	52.5	31	12.53	43.0	34	12.84	45.0
40	18.04	53.9	51	19.28	44.4	67	22.76	44.6
69	27.32	56.3	92	29.99	47.2	106	31.30	47.2

ions in general retard the ferric salt catalysis of hydrogen peroxide by shifting the equilibrium of the reaction in which ferric acid is produced.

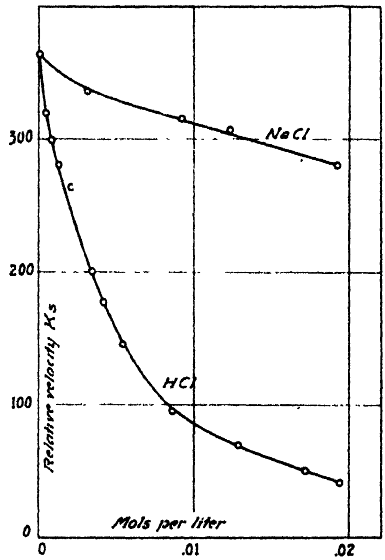

Fig. 2
Effect of Hydrochloric Acid and Sodium Chloride on Ferric Chloride Catalysis

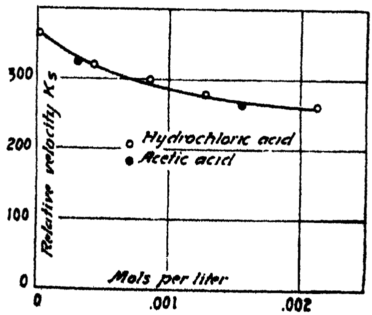

Fig. 3
Effect of Hydrochloric and Acetic Acids on Ferric Chloride Catalysis

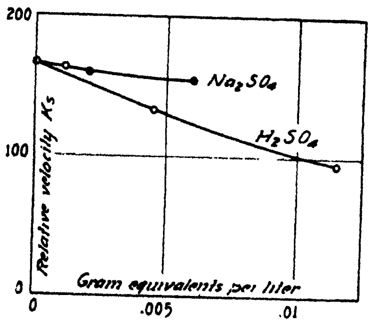

Fig. 4
Effect of Sulphuric Acid and Sodium Sulphate on Ferric Sulphate Catalysis

TABLE VII

Summary: Effect of Hydrochloric Acid on Ferric Chloride Catalysis

Mols per Liter of HCl	K_s
0	363
0.000425	319
0.00085	299
0.001275	280
0.002125	263
0.0034	200
0.00425	177
0.00538	146
0.008608	96
0.01291	70 2
0.01722	51.4
0.01937	42
0.02152	40.5

It must be remembered however that acid also affects the rate at which the catalyst is renewed so that it exerts two opposing effects. The facts indicate that the influence on the ferric acid equilibrium is of greater magnitude than that on the renewal of catalyst.

A further influence of acids having an ion in common with the catalyst such as sulphuric acid with the ferric sulphate, and hydrochloric acid with the ferric chloride, will be to slightly decrease the dissociation of the catalyst, and in that way exert a retarding effect.

TABLE VIII

Effect of Acetic Acid on Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter

C = mols per liter of CH_3COOH

t	x	K_s	t	x	K_s	Summary: Equivalents per Liter	Summary: K_s
1. C =	.0003		2. C =	.00155			
a =	41.24		a =	37.56		0	363
4.5	11.84	326	4	8.16	266	0.0003	326
9	20.31	327	9	16.08	269	0.00155	266
13	25.69	325	13	20.50	263		
			20	26.20	260		

It will be noted that equimolecular concentrations of acetic and hydrochloric acids in very dilute solution have approximately the same retarding effect.

TABLE IX

Effect of Sulphuric Acid on Ferric Sulphate Catalysis

$Fe_2(SO_4)_3$ = 0.006056 mol per liter

C = mols per liter of H_2SO_4

t	x	K_s	t	x	K_s	t	x	K_s
1. C =	.000575		2. C =	.0023		3. C =	00575	
a =	45.60		a =	45.90		a =	49.78	
4	5.34	163	5	6.51	133	5	5.16	95
8	11.59	159	13	13.49	127	12	11 00	90
16	19 69	153	26	23 78	122	26	20 34	88
29	28.76	149	38	29 68	119	40	27.50	87
40	33.74	146				57	33.79	86

Summary

Equivalents per Liter	K_s
0	166
0.00115	163
0.0046	133
0.0115	95

7d. Effect of Neutral Salts

Tables X to XIII, inclusive, show the effects of varying amounts of sodium chloride, mercuric chloride, sodium sulphate and sodium formate on the ferric chloride catalysis. The results are summarized in Table XIV and shown graphically in Fig. 5.

A salt having an ion in common with the catalyst retards the reaction, although comparatively slightly as is shown by the effect of sodium chloride on the ferric chloride catalysis and that of sodium sulphate on the ferric sulphate catalysis. (Table XV and Fig. 4.) The effect is undoubtedly due to the effect upon the ferric acid equilibrium of the increase in concentration of the chloride or sulphate ion, resulting in decreased dissociation of the catalyst and consequent formation of a smaller concentration of the intermediate

product. This effect is analagous to that of sodium acetate in decreasing the velocity of inversion of cane sugar by acetic acid.[1]

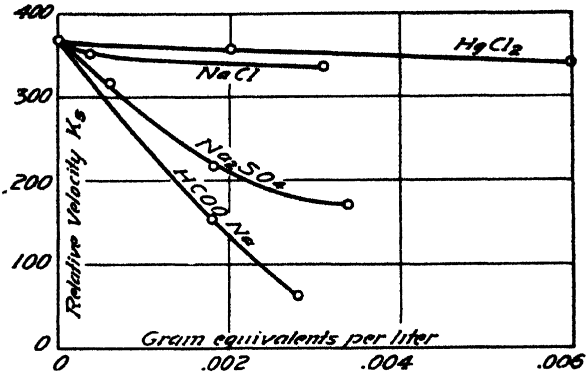

Fig. 5 Effect of Various Salts on Ferric Chloride Catalysis

TABLE X

Effect of Sodium Chloride upon Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter

C = mols per liter of NaCl

t	*x*	K_s	*t*	*x*	K_s	*t*	*x*	K_s
1. C=	.000385		2. C=	.000385		3. C=	.003076	
a=	44.51		*a*=	42.22		*a*=	41.22	
4	12.14	346	4	11.75	354	4	11.05	339
12	27.12	340	8	20.10	351	8	19.17	339
17	32.58	337	12	26.10	348	12	25.07	339
			17	31.09	341	17	30.18	337
4. C=	.003076		5. C=	.00923		6. C=	.0123	
a=	39.65		*a*=	39.14		*a*=	37.67	
4	10.49	333	4	9.86	315	4	9.42	312
12	23.85	333	8	17.41	319	8	16.37	309
17	28.81	331	12	22.92	319	12	21.53	307
			17	27.85	323	17	26.01	300
7. C=	.0192							
a=	38.80							
4	8.79	279						
8	15.65	280						
12	20.98	281						
17	25.78	280						

[1] Arrhenius: Zeit. phys. Chem., 4, 244 (1889).

Table XI

Effect of Mercuric Chloride on Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter
C = mols per liter of $HgCl_2$

t	x	K_s	t	x	K_s
1. C =	0.001		2. C =	0.003	
a =	48.30		a =	45.11	
3	10.48	354	3	9.44	340
6	17.69	330	6	16.67	334
10	25.49	325	10	23.94	329
18	35.42	319	18	33.03	318

Table XII

Effect of Sodium Sulphate on Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter
C = mols per liter of Na_2SO_4

t	x	K_s	t	x	K_s	t	x	K_s
1. C =	0.0003		2. C =	0.0009		3. C =	0.0017	
a =	46.95		a =	43.37		a =	46.42	
3	9.25	317	3	6.02	216	3	5.16	170
7	18.24	305	7	12.16	204	7	10.57	160
11	24.79	297	11	16.65	191	16	19.21	145
19	32.93	276	22	24.77	167	36	30.41	130

Table XIII

Effect of Sodium Formate on Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter
C = mols per liter of HCOO Na

t	x	K_s	t	x	K_s
1. C =	0.0018		2. C =	0.0028	
a =	42.86		a =	45.08	
4	5.63	153	8	4.87	62
19	16.15	108	20	9.55	52
45	25.33	81	33	15.44	55
82	32.58	75	80	21.50	35

TABLE XIV

Summary: Effect of Neutral Salts on Ferric Chloride Catalysis
$FeCl_3$ = 0.002974 mol per liter
Eq = equivalents per liter

$HgCl_2$		NaCl		Na_2SO_4		HCOONa	
Eq	K_s	*Eq*	K_s	*Eq*	K_s	*Eq*	K_s
0	366	0	366	0	366	0	366
		0.000385	350	0.0006	317	0.0018	153
0.002	354	0.003076	336	0.0018	216	0.0028	62
		0.00923	315	0.0034	170		
0.006	340	0.0123	312				
		0.0192	279				

TABLE XV

Effect of Sodium Sulphate on Ferric Sulphate Catalysis

$Fe_2(SO_4)_3$ = 0.006056 mol per liter
C = mols Na_2SO_4 per liter

t	*x*	K_s	*t*	*x*	K_s
1. C =	0.001		2. C =	0.003	
a =	43.31		*a* =	43.19	
6	8.53	159	6	8.26	154
14	16.88	153	14	16.36	148
26	25.41	148	26	24.83	143
45	33.37	142	45	32.81	137

Summary

Equivalents per Liter	K_s
0	166
0.002	159
0.006	154

That a less dissociated chloride has a similar though very small effect on the ferric chloride catalysis is shown by the action of mercuric chloride on the reaction. Although it has been shown that a peroxide of mercury[1] is formed by and re-

[1] Bredig and Weinmayr: Loc. cit.

acts with hydrogen peroxide, mercuric chloride alone has no effect whatever nor, according to Professor Walton, has mercuric cyanide. This fact is undoubtedly connected with their very small dissociation.

Sodium sulphate and sodium formate retard the ferric chloride catalysis much more than does an equivalent concentration of sodium chloride, the salt of the weakest acid showing the greatest retarding effect. Sodium acetate exerts a similar marked effect; concordant quantitative results were not obtained owing to the formation of a precipitate of basic ferric acetate during the reaction. These results are in harmony with the fact already noted that the ferric salt of a strong acid is a more effective catalyst than that of a weak acid.

When sodium formate for example is present with the ferric chloride an equilibrium between ferric chloride and ferric formate must result with two consequent equilibria between the ferric salts and ferric acid. The retardation then must be due in some way to the presence of the ferric formate as a catalyst. In the first place formic acid is a product of its action. This is a relatively weak acid and its dissociation is still further decreased by the hydrochloric acid already present. The effect of such a decreased hydrogen ion concentration will be two-fold: (1) it will shift the equilibrium with a resulting greater concentration of ferric acid and (2) it will retard the rate at which catalyst is renewed. It has already been pointed out that although these two effects are opposed the effect on the first equilibrium is of greater magnitude. It thus appears that the influence of sodium formate cannot be adequately explained by the change in hydrogen ion concentration. The introduction of formate ion must, therefore, be the cause of the retardation. The same considerations will hold for the effect of sodium sulphate on the ferric chloride catalysis and for the action of ferric sulphate as a catalyst.

According to our conception of hydrolysis, the three salts ferric chloride (or nitrate), ferric sulphate, and ferric

formate, are hydrolyzed more readily and to a greater extent, the weaker the acid of which they are salts. It has already been demonstrated that the basic salt or colloidal hydroxide formed by hydrolysis is an inactive substance; it may, therefore, be easily possible that in the case of ferric salts of the weaker acids correspondingly more of the catalyst is converted into this inactive substance, resulting in the retardation shown, or that the total influence may be the resultant of this effect and the hydrogen ion effect combined.

8. The Joint Effect of Two Catalysts

When two substances which individually accelerate a reaction are allowed to act simultaneously, the total velocity may be equal to the sum of the separate velocities, as in the case of the action of a mixture of colloidal gold and colloidal platinum upon the decomposition of hydrogen peroxide.[1] On the other hand, it often varies widely from the calculated additive effect. For example, the oxidation of hydriodic acid by hydrogen peroxide[2] is accelerated individually by the following: Ferrous sulphate, copper sulphate, and zinc sulphate; sulphuric, molybdic, and tungstic acids. The table below shows the effect of mixing the catalysts.

Mixture	Calc. additive V.	Observed V.
(*a*) $FeSO_4 + H_2MoO_4$	314	321 practically additive
(*b*) $CuSO_4 + H_2MoO_4$	247	250 practically additive
(*c*) $FeSO_4 + H_2WO_4$	369	270 retardation
(*d*) $FeSO_4 + CuSO_4$	315	350 acceleration
(*e*) $H_2SO_4 + H_2WO_4$	275	370 acceleration

Brode assumes the retardation in case (*c*) to be due to the formation of an inactive complex between the ferrous sulphate and tungstic acid. The accelerating effect of cases (*d*) and (*e*) has not been explained.

Again, the reaction between potassium iodide and potassium persulphate is accelerated by ferrous sulphate, by

[1] M. et Mme. Henri: Comptes rendus Soc. Biol., 55, 864 (1903).

[2] Brode: Loc. cit.

copper sulphate, and by zinc sulphate,[1] in proportion to their concentration. A mixture of ferrous and copper sulphates accelerates more than the calculated additive amount, while a mixture of zinc and ferrous sulphates occasions a velocity smaller than the calculated. In a similar manner, copper sulphate and mercuric sulphate when mixed accelerate the oxidation of aniline by sulphuric acid to a greater extent than is indicated by the sum of their separate effects.[2]

Several experiments were performed to determine the result of mixing some of the catalysts used in this study. The data, which are given in Table XVI, may be summarized as follows:

Catalyst	Calculated K_s	Observed K_s
$Fe_2(SO_4)_3$ alone	—	200
$Fe(NO_3)_3$ alone	—	293
$Fe_2(SO_4)_3 + Fe(NO_3)_3$	493	210
$Fe_2(SO_4)_3$ alone	—	166
$FeCl_3$ alone	—	361
$Fe_2(SO_4)_3 + FeCl_3$	527	196
$CuSO_4$ alone	—	8
$Fe_2(SO_4)_3 + CuSO_4$	174	467

Two ferric salts mixed do not cause a velocity as great as the sum of the two separate effects. It thus appears that possibly the sulphate ion has a still further specific retarding influence that is not accounted for in the discussion of the previous results. Whether or not it is due to the formation of an inactive complex, as Brode believed in the case of ferrous sulphate and tungstic acid, is problematical.

Copper sulphate accelerates the ferric sulphate catalysis to a very marked degree. In this case the aforementioned retarding effect of sulphate ions must be greatly overbalanced by an effect of the copper ions, which apparently are very active in catalyzing the interaction between hydrogen peroxide and ferric acid.

[1] Price: Zeit. phys. Chem., 27, 474 (1898).
[2] Bredig and Brown: Ibid., 46, 502 (1903).

TABLE XVI

The Joint Effect of Two Catalysts

C = mols per liter

t	x	K_s	t	x	K_s	t	x	K_s
1. $Fe_2(SO_4)_3$ alone			2. $Fe(NO_3)_3$ alone			3. $Fe_2(SO_4)_3$ 0.01923 + $Fe(NO_3)_3$ 0.00243		
C	= .01923		C	= .00243				
a	= 44.35		a	= 42.78		a	= 41.08	
3	5.73	200	3	7.85	293	3	5.54	210
7	11.89	194	7	15.79	286	7	11.57	205
12	18.10	189	12	22.90	277	12	17.40	199
19	24.68	186	18	28.60	266	19	23.64	196
31	32.14	181	27	33.75	250	32	30.94	190
4. $Fe_2(SO_4)_3$ alone			5. $FeCl_3$ alone C = .002974			6. $Fe_2(SO_4)_3$ 0.006056 + $FeCl_3$ 0.002974		
C	= .006056							
a	= 42.20		a	= 44.59		a	= 41.84	
4	5.97	166	2	6.83	361	4	6.94	196
12	15.26	162	5	14.75	349	10	15.16	195
23	23.91	157	8	21.09	347	19	23.97	194
33	29.25	156	14	29.78	341	33	32.12	192
			21	35.65	332			
7. $CuSO_4$ alone			8. $Fe_2(SO_4)_3$ — .006056 + $CuSO_4$ — .001541			9. Duplicate of (8)		
C	= .001541							
a	= 50.51		a	= 41.16		a	= 44.64	
144	11.70	7.8	4.5	15.64	460	5	18.77	473
329	23.75	8.4	8	21.91	412	11	27.99	389
			13	27.43	367	19	34.21	332
			20	32.03	327		Mean	467

9. The Effect of Miscellaneous Anticatalysts

In the preceding paper it was shown that alcohol and glycerol may be used as solvents without apparent oxidation when hydrogen peroxide is decomposed by sodium iodide. However, 1.6% of ethyl alcohol or 3% of glycerol are sufficient to prevent any evolution of oxygen whatever when ferric salts are used as catalysts. Gelatine, which only slightly retards the decomposition with sodium iodide, inhibits al-

together the action of ferric salts, as do urea, sugar, acetanilid, and acetaldehyde.

The effect of small amounts of alcohol on the ferric chloride catalysis is shown in Table XVII. Since the amount of oxygen evolved is not sufficient to account for complete decomposition of the hydrogen peroxide into oxygen and water, the results are of relative value only. They are sufficient to show, however, that only traces of this substance are necessary to greatly retard the reaction. It is clear that two influences are at work: (1) An oxidation of the alcohol to acetic acid (reference to such oxidations under the influence of ferric salts as catalysts has been made in the introduction,) and (2) the retarding effect of acetic acid already demonstrated. It should be noted that although the constants are irregular, the retarding effect is in general of the same order of magnitude as that of acetic acid.

The slight effect of acetanilid on the sodium iodide catalysis is shown in Table XVIII.

Mols per Liter Acetanilid	K_s
0	128.7
0.0057	124
0.0114	120

This substance has been frequently mentioned as a preservative for hydrogen peroxide;[1] the results with these two catalysts lead to the thought that the "spontaneous" decomposition of hydrogen peroxide may be due to traces of iron salts.

The writer desires to take this opportunity for expressing his appreciation to Professor J. H. Walton, at whose suggestion this research was undertaken, and under whose direction it was carried out, for his kindly interest and guidance during its progress.

[1] LaWall: Am. Jour. Pharm., 78, 582.

TABLE XVII

Effect of Ethyl Alcohol upon Ferric Chloride Catalysis

$FeCl_3$ = 0.002974 mol per liter
Ethyl Alcohol—C = mols per liter

t	x	K_s	t	x	K_s	t	x	K_s
1. C=	.0001672		2. C=	.0003344		3. C=	.000836	
a=	44.87		a=	46.89		a=	44.27	
3	9.43	341	5	12.44	268	4	9.33	257
7	19.26	348	9	21.80	302	8	17.18	267
11	26.39	350	14	29.09	301	12	23.14	268
17	33.41	349	20	34.69	292	21	31.50	257
22	37.03	345						
4. C=	.001338		5. C=	.001672		6. C=	.003344	
a=	44.40		a=	42.55		a=	47.38	
4	7.51	201	3	5.71	208	7	6.76	95.5
8	15.17	224	7	12.37	213	12	13.27	112
13	22.70	237	12	19.11	216	19	21.44	137
23	31.90	239	19	25.50	209	30	29.80	143
			30	31.34	193	44	34.39	128
7. C=	.00836		8. C=	01672				
a=	48.98		a=	50.11				
18	4.51	23.3	31	0.61	1.71			
30	10.54	35.1	99	9.13	8.82			
98	33.65	51.1						

TABLE XVII—SUMMARY

Alcohol	
C	K_s
0	363
0.0001672	341
0.0003344	268
0.000836	257
0.001338	201
0.001672	208
0.003344	96
0.00836	23
0.01672	—

TABLE XVIII

Effect of Acetanilid on Sodium Iodide Catalysis

NaI = 0.02053 mols per liter
C = mols acetanilid per liter

t	x	K_s	t	x	K_s
1. C =	.0057		2. C =	.0114	
a =	44.58		a =	45.58	
5	5.94	124	5	5.86	120
10	11.10	124	10	11.00	120
19	18.70	124	19	18.63	120
28	24.61	125	28	24.66	121
43	31.60	125	43	31.73	122

10. Summary

1. It has been shown that ferric salts accelerate the decomposition of hydrogen peroxide to a greater degree than sodium iodide in equivalent concentration. For dilute solutions of the chloride and nitrate, the velocity is proportional to the concentration. Ferric sulphate is less effective than the chloride and nitrate.

2. The catalytic effect may be explained by the formation of an intermediate product, which appears to be represented as follows:

$$(1)\ 2FeR_3 + 3H_2O_2 + 2H_2O \rightleftarrows 2H_2FeO_4 + 6HR$$
$$(2)\ 2H_2FeO_4 + 3H_2O_2 \longrightarrow 2Fe(OH)_3 + 2H_2O + 3O_2$$
$$(3)\ 2Fe(OH)_3 + 6HR \rightleftarrows 2FeR_3 + 6H_2O$$

in which (2) is the measurable reaction. Constants were obtained for the expression for a monomolecular reaction.

3. The specific reaction velocity decreases as the reaction proceeds, due to hydrolysis of the catalyst. Such products of hydrolysis as colloidal ferric hydroxide or the basic salts have no catalytic effect.

4. The addition of free acid retards the reaction, apparently by reducing the concentration of the intermediate product. Salts having an ion in common with the catalyst retard the decomposition by decreasing the dissociation of the catalyst. The slightly dissociated mercuric chloride has a very small influence.

5. Sodium sulphate, acetate, and formate delay the reaction apparently through the hydrolysis of a portion of the resulting ferric salt.

6. A mixture of ferric sulphate with ferric chloride or ferric nitrate does not accelerate the reaction to so great an extent as would be indicated by the sum of their separate effects. Copper sulphate greatly hastens the ferric sulphate catalysis.

7. Alcohol, which is oxidized in the presence of a ferric salt, acts anticatalytically owing to the formation of acetic acid. Glycerine, sugar, gelatine, urea, and acetanilid also act as anticatalysts.

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University of Wisconsin
Madison, July 1920

THE LAW OF PROBABILITY APPLIED TO THE FORMATION OF FATS FROM CARBOHYDRATES[1]

BY EDGAR J. WITZEMANN

In considering the possible mechanism of the formation of fatty acids in living organisms there are certain outstanding fundamental facts which must be taken into account. Five important facts of this kind follow:

(1) The fats in plants are almost altogether synthesized from carbohydrates. The same is largely true in most animals.

(2) The carbohydrates involved are largely hexoses or their polymers, since these are most abundant. In animals glucose and glycogen alone are involved so far as is known.

(3) The fatty acids occurring in plants and animals are almost solely composed of those acids having an even number of carbon atoms in their chains.

(4) The fat stores are composed almost entirely of acids having long chains with eighteen carbon atoms.

(5) Oleic acid is the principle unsaturated acid occurring in vegetable and mineral fats. The other unsaturated acids are quantitatively of isolated or much less importance.

Taking the above facts into account two general types of hypotheses have been developed concerning the chemical mechanism of the formation of fatty acids.

A. They are built up mainly from short carbon chains (less than six).

B. They are built up mainly from units of six carbon atom chains.

In the first hypothesis (3) above, namely that the acids contain an even number of carbon atoms, has received undue emphasis. Most of the meagre direct chemical data has been marshalled in support of this type of hypothesis. Thus the

[1] Contribution from the Otho S. A. Sprague Memorial Institute, Rush Medical College, Chicago, Ill.

recent theory of Magnus-Levy[1] is based on the intermediate formation of acetaldehyde in order to explain the formation of butyric, caproic and acetic acids in liver autolysis. The sugar is thought to decompose into lactic acid which in turn gives carbon dioxide, hydrogen and acetaldehyde. Buchner and Meisenheimer,[2] Nencki,[3] H. St. Raper[4] and Euler[5] have advocated somewhat similar ideas, which were extended in some respects, especially by Euler. Ida Smedley[6] pointed out the possible importance of the condensation of acetaldehyde with pyruvic acid thus, for example:

(1) $CH_3.COH + CH_3COCO_2H \longrightarrow CH_3CHOHCH_2COCO_2H,$
(2) $CH_3CHOHCH_2COCO_2H + O \longrightarrow CH_3CHOHCH_2CO_2H + CO_2,$
(3) $CH_3CHOHCH_2CO_2H - H_2O \longrightarrow CH_3CH : CHCO_2H.$

Although the above types of hypotheses all represent reactions that can or do take place they fail in important respects to account for certain facts. For instance, why should the greater portion of fats be made up of C_{18} acids if acetaldehyde and pyruvic acid are intermediate compounds in their formation? Why should not intermediate short chain acids especially occur more largely if they are intermediate stages in the formation of the typical C_{18} acids?

In emphasizing the fact that fatty acids occurring in nature contain only an even number of carbon atoms, the other fundamental facts given above are disregarded. These facts may be graphically summarized by the statement that six carbon atom sugars give rise to eighteen carbon atom fatty acids. This statement gives emphatic emphasis to the arithmetical relation of the number of carbon atoms in the compound transformed and in the final product. Emil Fischer[7] has utilized this fact clearly in his hypothetical interpretation of the formation of fats from sugar.

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[1] Arch. Anat. Phys., Phys. Abt., **1902**, 365.
[2] Ber. deutsch. chem. Ges., **43**, 1773 (1910).
[3] Ibid., **10**, 1033 (1877).
[4] Proc. Chem. Soc., **23**, 235 (1907); Jour. Physiol., **32**, 216 (1906).
[5] Pflanzenchemie, II, 212 (1909).
[6] Zentr. Physiol., **26**, 915 (1912); Jour. Physiol., Dec. (1912).
[7] Untersuchung über Kohlenhydrate und Fermente, 110 (1884–1903).

"In order to derive stearic and oleic acids, which occur combined with glycerol in most fats, from sugar, it is only necessary to assume that three molecules of the latter are joined through their aldehyde groups as occurs with formaldehyde in the synthesis of sugar. Then a molecule of 18 carbon atoms would result in which only a transposition and removal of oxygen is necessary in order to produce these acids." * *

"For palmitic acid with 16 carbon atoms, which also occurs abundantly in fats, the same explanation would be adequate if one molecule of hexose and two molecules of pentoses which occur so abundantly in plants were brought together; moreover, it is also possible that it is formed from a system with 18 carbon atoms by splitting." * * * "If the sugar molecule is not completely broken up in the formation of fat, which I consider improbable, one may expect that the sugars with different carbon content will give rise to differently constituted fats."

Little or no laboratory experimental data is at hand to support this hypothesis but some of the biological data seems ummistakably clear in its support. The transformation of sugars and carbohydrates of unripe oil seeds into fat[1] appears to be quite direct. The results of Gierke's experiments[2] give even clearer support. He found in guinea pigs that fat tissue which normally is free from glycogen on the second and third days, when they are heavily fed on carbohydrates, contains much glycogen on the eighth day. In fasting or in extended feeding periods the glycogen disappeared from the fat cells by the fourteenth day.

However, this hypothesis, even in the absence of definite chemical data, commends itself for its simplicity and it was therefore of interest to learn whether there are any other considerations that can be enlisted in its support.

If fatty acids are built up two carbon atoms at a time, as suggested by the first hypothesis, it follows that since the over-

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[1] Cf. for instance F. Czapek: Biochemie der Pflanzen, 2nd Ed , p 742, et seq.

[2] Verh. d. pathol. Ges., 1906, 182.

whelming proportion of all fatty acids found everywhere are C_{18} acids, there must be a reason for the synthesis proceeding to this point and then stopping just there. Such a reason could be supplied by a sufficiently sharp change in some physical property that regulates the synthesis. But such a sharp change is not known. In fact the fatty acid series is one of the homologous series in organic chemistry most noted for regular and gradual transition in physical properties on moving up or down the series. In the absence of such a change or discontinuity in properties the synthesis of fatty acids by the addition of two carbon atoms at a time becomes amenable to the law of probability for any given set of chemical conditions. Thus if we accept the statistical fact of C_{18} acids being in the preponderance in fats these acids become our "bull's eye" in discussing their formation from this point of view.

Accurate information as to the quantitative occurrence of the various fatty acids is not available, but a qualitative estimate on the basis of such information as is obtainable from the handbooks, etc., gives a curve such as that represented by the solid line in Fig. I. Now, on connecting up the points which represent the relative abundance of the various acids instead of obtaining a smooth descending curve on both sides of C_{18}, the curve shows prominences at C_{12}, C_{24}, etc., which do not conform to the typical probability curve. If, however, the prominences are connected, as in the dotted line in the figure the typical probability curve is obtained. Moreover, the number of carbon atoms at the prominences are all divisible by six and this suggests the direct relation to the parent hexose sugars provided by Emil Fischer's hypothesis.

Accordingly, the data when assembled and judged in terms of the law of probability, appear to be against the first type of hypothesis and to support the second hypothesis.

Moreover by this view of it it becomes possible to explain why the major portion of fatty acids should have eighteen carbon atoms. If these acids are built up six carbon atoms at a time the first complex C_{12} is still sufficiently soluble either as the disaccharide or as the C_{12} acid to react rapidly with

another C_6 unit to give C_{18} either as the trisaccharide or the C_{18} acid. But in both cases the C_{18} compound is much less soluble, and presumably less reactive, than the smaller C_6 or C_{12} units so that higher acids would not be formed rapidly from C_{18} units. Here we have a sufficiently large change in physical properties when dealing with 6 carbon units to easily account for the non-formation of large amounts of fatty acids containing more than eighteen carbon atoms.

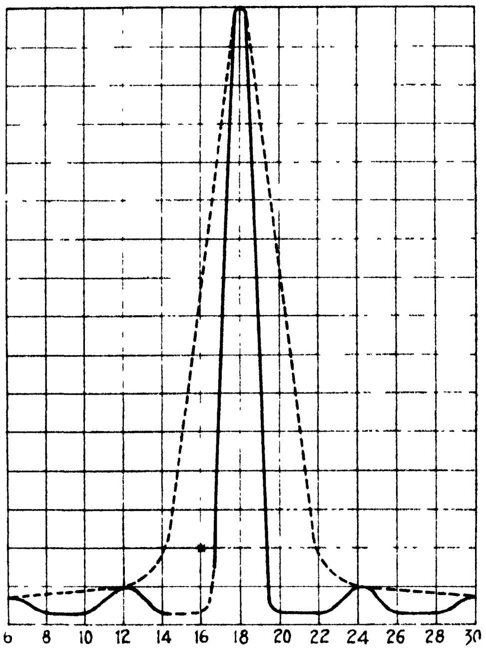

Fig. 1

The smaller occurrence of the intermediate acids, such as C_{10}, C_{14}, C_{16}, etc., may be due to the fact that they are formed from higher unsaturated acids by loss of two or more carbon atoms or by such syntheses as those involved in the first hypothesis. The apparent anomalously large occurrence of palmitic acid (C_{16}) may be accounted for by the known fact mentioned above that oleic acid undergoes a transforma-

tion at the α- and β-carbon atoms to give palmitic acid and another product. This type of reaction occurs for instance in the treatment of oleic acid with strong alkali.

In conclusion, it needs merely to be said that even the qualitative application of the law of probability appears to rationalize the problem of the mechanism of the formation of fatty acids from sugars in an interesting way. If true, the suggestion herein given constitutes a different biological application of the probability law from that known in biology as Quetelet's Law of Fluctuating Variation.

THE OXIDATION AND LUMINESCENCE OF PHOSPHORUS. I

BY HARRY B. WEISER AND ALLEN GARRISON

The Behavior of Phosphorus in Pure Oxygen

The connection between the oxidation and luminescence of phosphorus was recognized by Berthollet[1] in 1797. He observed the emission of light when phosphorus was exposed to air or oxygen and records that he found oxygen necessary for the production of light. Certain investigators claimed, however, that phosphorus glowed in other gases such as nitrogen and hydrogen and even in a vacuum. These observations led Berzelius[2] to ascribe the luminescence to vaporization of phosphorus. This conclusion has been proven erroneous by the investigations of Fischer,[3] Schrötter,[4] Müller[5] and Joubert,[6] who have shown that luminescence never occurs in the absence of oxidation.

Although oxygen is necessary for the luminescence of phosphorus, the interesting observation has been made that phosphorus does not glow in oxygen under certain conditions. As early as 1788 Fourcroy[7] recorded that phosphorus and pure oxygen at 760 mm pressure and below 27 degrees did not react, whereas rapid oxidation took place in the air under similar conditions. A little later van Marum[8] found that phosphorus glowed much brighter in diluted than in ordinary air; and that it would ignite even at very low pressure

[1] Jour. de l'École polyt., 3, 274 (1797).

[2] Lehrbuch der Chemie, 5th Edition, 1, 195; cf. Marchand: Jour. prakt. Chem., 50, 1 (1850).

[3] Jour. prakt. Chem., 35, 342 (1845); 39, 48 (1846).

[4] Ibid., 58, 150 (1853).

[5] Ber. deutsch. chem. Ges., 3, 84 (1870).

[6] Thèses sur la phosphorescence du phosphore, Paris (1874).

[7] Mémoires de l'Académie des Sciences (1788).

[8] Verhandelingen uitgegeeven door Teylers Tweede Genootschap, 10, (1798).

providing it was covered with a little wadding. In 1813 Bellani[1] found that phosphorus will luminesce in pure oxygen just as it does in air, providing the oxygen pressure is reduced. Müller[2] confirmed Fourcroy's observation that phosphorus does not glow in pure oxygen. He filled a flask with the gas at ordinary pressure; added a piece of phosphorus; and sealed it up for 2.5 months. The flask was opened under water and no change in volume could be noted. Since these observations apparently contradict the Law of Mass Action, it is not surprising that a number of chemists have investigated the connection between the velocity of oxidation of phosphorus and the oxygen concentration.

In a systematic investigation of the factors affecting the luminescence of phosphorus, Joubert[2] established the existence of a so-called "boundary pressure" of oxygen above which no oxidation or luminescence takes place. The method employed consisted in the determination at a definite temperature of the pressure at which the phosphorus just started to glow. The determinations were carried out in an apparatus which consisted essentially of a water-jacketed tube attached to a Gay-Lussac manometer. In the tube he placed a piece of phosphorus and oxygen under a pressure which allowed no oxidation. After adjusting the temperature to the desired point he withdrew mercury from the manometer until the phosphorus just glowed. He then increased the pressure until the luminescence disappeared and after a time repeated the operation. The average of six such observations which differed by not more than 10–15 mm he considered as the boundary pressure. Although there was but little difference in the boundary pressure observed with the same phosphorus and oxygen, the experiments made at the same temperature with different samples of the two showed variations of as much as 100 mm. This variation is shown from the two series of experiments recorded in Table I.

[1] Bull. de Pharm., 1813, 489.
[2] Loc. cit.

TABLE I

I		II	
Temp.	Partial pressure of oxygen	Temp.	Partial pressure of oxygen
11.5	580	11.0	495
14.2	650	15.2	570
18.0	730	16.0	595
19.5	760	—	...

Joubert is undecided whether to attribute this variation to the condition of the phosphorus or the oxygen. Moreover, he does not take into account the possible effect of moisture since he does not state whether wet or dry oxygen was employed.

Ikeda[1] studied the velocity of oxidation of phosphorus in moist air and found that it was approximately proportional to the partial pressure of the oxygen up to a certain point, above which the velocity of oxidation decreased. This investigation was repeated by Ewan,[2] who pointed out the influence of the rate of evaporation of the phosphorus on the reaction velocity:

"The increase of the velocity constant shows that at low pressures the reaction proceeds somewhat faster than would be expected if its velocity was simply proportional to the pressure. Apparently the cause of this relation is to be sought in the fact that substances vaporize to the gaseous state more rapidly at low than at high pressures. It can hardly be doubted that the reaction takes place between phosphorus vapor and oxygen and also, if it is permissible to consider the phosphorescence as an indication of the location of the reaction, the latter takes place quite close to the surface of the phosphorus as long as the oxygen pressure is not too low. Doubtless one may assume, therefore, that the phosphorus vapor which is evolved at the surface of the phosphorus oxidizes at once and therefore that the velocity of the

[1] Jour. Coll. Sci. Tokyo Imp. Univ., **6**, 43 (1893).

[2] Zeit. phys. Chem., **16**, 315 (1895).

reaction will be proportional to the rate of evaporation of the phosphorus.

"Assuming this proportionality it is quite possible to give a consistent and fairly satisfactory explanation of the course of various reactions that are apparently quite abnormal."

Ewan also studied the oxidation of phosphorus in both moist and dry oxygen and expressed his results by means of curves after correcting the reaction velocities to constant rate of evaporation of phosphorus: "Obviously the values obtained lie on a straight line which passes through the origin. The corrected velocities are therefore proportional to the pressure. At pressures above 500 mm this proportionality no longer holds; the velocity decreases rapidly and becomes zero at about 700 mm."

Ewan determined the point at which oxidation just ceased by noting whether there was any change in the manometer at a given temperature and pressure. In this way he found that at a temperature of 20.4° to 20.7° and at a pressure of 695.6 mm no oxidation took place in moist oxygen in 22 minutes; but a very slight oxidation was noted after 50 minutes. Again, at a temperature of 20.43° to 20.64° no oxidation was observed at 671.1 mm in 43 minutes.

With oxygen dried by phosphorus pentoxide Ewan obtained no very regular curve for the rate of oxidation. The reaction velocity was slower and the boundary pressure was lower than with moist oxygen. Thus at a temperature of 20.87° to 21.26° at a pressure of 377 mm no oxidation was observed after 70 minutes, but it was noted at a pressure of 201.6 mm after 110 minutes. Baker[1] observed no oxidation in oxygen dried by phosphorus pentoxide, but it is not known whether he worked at low pressures.

Centnerszwer[2] determined the boundary pressure with moist oxygen at 20° and found it to be 567 mm. Like Joubert, he observed the point at which luminescence started

[1] Phil. Trans., **178**, 571 (1888).

[2] Zeit. phys. Chem., **26**, 1 (1898).

while diminishing the pressure with an air-pump. He studied the effect of various factors on the pressure necessary for the emission of light. Among those which had no effect were the extent of the surface of phosphorus exposed and the volume of the oxygen. He found, however, that the rate at which the pressure was lowered had a marked influence on the glow pressure. "It was found that the more slowly the evacuation was carried out the higher was the glow pressure. The difference amounted to as much as 50 mm in extreme cases. The most constant values were obtained when the velocity of the pressure change was made so great that the glow pressure could be caught accurately within 1 mm. This was gotten when the evacuation lasted 45 to 60 seconds."

Centnerszwer observed another interesting phenomenon which he does not explain: "If the pressure is lowered to a pressure 50 mm above the glow pressure and the evacuation stopped, an intermittent luminescence is observed after a little while. The glowing is repeated quite regularly at intervals of approximately 20 seconds. If the pressure is lowered further, the periods become shorter until the light finally begins to run on the piece of phosphorus; it moves regularly from the top to the bottom like a number of bands passing along the stick of phosphorus. If the pressure is diminished still further the phosphorus glows continuously. Unfortunately, I have not had the time to investigate further this interesting phenomenon and the circumstances which are responsible for its appearance."

In the light of the above observation it is evident that the glow pressure observed by Centnerszwer is somewhat lower than the real boundary pressure. It will be noted that Centnerszwer's value at 20° is much lower than that found by Joubert by the same general method of procedure. Centnerszwer attributed this to the effect of ozone, a trace of which was found to cause phosphorus to luminesce in pure oxygen at atmospheric pressure:[1] "This circumstance explains the fact that Joubert in his experiments with pure

[1] Cf. Chappuis: Bull. Soc. chim. Paris, **35**, 419 (1881).

oxygen found a glow pressure much greater than I and that Ewan recorded a higher pressure for the beginning of oxidation than was found in my experiments described above. Both authors rarefied their oxygen repeatedly before the experiments and thereby have occasioned the formation of ozone; in consequence a glowing or oxidation occurred at a higher pressure than in the absence of ozone. However, if the apparatus is filled by displacement of water instead of first exhausting it, another view of the phenomenon is obtained."

Russell[1] has made a careful investigation of the oxidation of phosphorus in moist and dried oxygen and an examination of the products formed. As a source of oxygen he used potassium chlorate in a portion of the apparatus so arranged that he could pass the gas either through concentrated sulphuric acid or phosphorus pentoxide as drying agent. His procedure was to cool the bulb containing phosphorus in ice water; generate oxygen by heat; pass the gas through the desired drying agent; and adjust to the desired pressure. The temperature was then raised to approximately 15° and the rate of change of pressure noted on the manometer. The effect of moisture on the velocity of oxidation was first studied; and he found that oxygen dried by sulphuric acid reacts more quickly than the moist: "These experiments show that an increase in amount of water increases the velocity of oxidation, but that a maximum is soon reached after which further additions have a retarding influence. Many attempts were made to determine the limits within which the most favorable quantity of water lay, but with only partial success. The general result was that oxidation was most rapid when phosphorus and oxygen had been dried over sulphuric acid and the phenomena of oxidation in these circumstances were carefully observed."

Russell carried out a series of experiments in which the initial pressure of the oxygen was between two and three atmospheres. His results failed to confirm the usual statement that phosphorus reacts with oxygen only under low pressures:

[1] Jour. Chem. Soc., 83, 1263 (1903).

"Moderately dried [with sulphuric acid] phosphorus and oxygen react under all pressures tried and the phenomena of 'false equilibrium' are not seen. The reaction may be divided into two stages; in the first, oxidation is slow and accompanied by a very feeble glow, the action being apparently unimolecular. The second stage begins when the pressure falls below about 500 mm. Oxidation is continually accelerated until all the oxygen is absorbed but no simple expression could be found connecting the velocity of the reaction with the pressure of oxygen. The glow is very bright and phosphorus pentoxide is formed. No satisfactory explanation of the second stage can yet be offered."

Russell found a boundary pressure with wet oxygen, however. In one experiment he observed no oxidation in wet oxygen under high pressure even after six months. "The oxidation does not begin until the oxygen present is less than about 500 mm. When it does take place it is slower and is much retarded during the earlier part of the reaction. The retardation is explained as being due to a protective film formed in some probably physical manner by the water on the phosphorus."

Jorissen and Ringer[1] attribute Russell's failure to obtain a boundary pressure with oxygen dried with sulphuric acid to the fact that he "let the oxygen prepared by heating pure chlorate or permanganate of potassium, enter the apparatus without taking care to exclude possible traces of ozone or oxygen ions." Reference has already been made to Centnerszwer's view of the effect of ozone on boundary pressure. Accordingly, the oxygen used by Jorissen and Ringer in their investigation was prepared some days before using and freed from traces of ozone. Their method of observation was essentially the same as that of Ewan. A portion of their data has been summarized in Table II.

The above survey of the work of different investigators on the behavior of phosphorus in oxygen under various conditions discloses a number of conflicting observations: Thus,

[1] Chem. News, **92**, 150 (1905).

TABLE II
The Boundary Pressure of Oxygen
(Temperature 15°)

Nature of oxygen	Oxygen pressure	
	No oxidation	Oxidation
Saturated with water vapor	626	593
Saturated with water vapor	601	591
Saturated with water vapor	637	602
Dried with calcium chloride	609	592-534
Dried with calcium chloride	585	538
Dried with phosphorus pentoxide	445	330

Russell found no boundary pressure whatsoever for phosphorus in pure oxygen dried by sulphuric acid and Baker observed no oxidation at all in pure oxygen dried by phosphorus pentoxide, whereas both Ewan and Jorissen showed a boundary pressure to exist in oxygen dried in different ways. Moreover, different investigators obtained quite different values for the boundary pressure at the same temperature in both moist and dry oxygen. No satisfactory explanation has been offered for the existence of a boundary pressure in dry oxygen and Russell's assumption that a film of water protects the phosphorus in moist gas does not explain why there is no oxidation above a certain partial pressure of oxygen whereas oxidation takes place below this partial pressure of oxygen the total gas pressure remaining constant. Nor is any satisfactory explanation offered for the fact that with the same phosphorus and oxygen the boundary pressure is apparently influenced by the rate at which the oxygen pressure is reduced. It would seem therefore that further data are necessary to determine the relation between phosphorus and oxygen, excluding materials such as ozone, which apparently influence the reaction.

Experimental

Experiment 1.—As previously pointed out, a fairly definite boundary pressure is obtained in the oxidation of

phosphorus in moist oxygen. If this is due to the presence of a film of moisture as Russell assumes, it would seem possible to remove the film in some mechanical way and so produce glowing. Accordingly, the following experiment was carried out. In the experiments purified and redistilled white phosphorus was employed. The oxygen used was obtained from a tank of electrolytic oxygen that analyzed 97 percent pure.

A small piece of phosphorus was fixed on a glass rod and mounted in an atmosphere of oxygen saturated with moisture. A Woulff bottle having three openings was used for the purpose. In one opening was placed a two-holed rubber stopper through one hole of which the rod bearing the phosphorus was inserted and through the other hole a glass rod flattened at the end. The latter served as a mechanical scraper. Through a second opening in the bottle was inserted two tubes for filling the jar with oxygen; and through the third opening was inserted a thermometer.

After filling the bottle with oxygen, it was placed in a refrigerator and brought to a temperature of 15°. At this temperature and atmospheric pressure no oxidation or luminescence was observed. If, however, the surface of the phosphorus was scraped with the glass rod an occasional spark appeared which, after a time, became a continuous glow in a spot where the scraping took place. This glow spread rapidly until the whole surface was luminous. The experiment was repeated at 10° with similar results except that a more vigorous scraping was necessary to start the reaction.

The result of this experiment is not convincing. It may readily be seen that the mechanical removal of any film which may exist must involve friction and thus a local heating. Hence it can not be said with any degree of certainty, that a film has been removed exposing pure phosphorus to the attack of oxygen. It is quite as probable that enough local heating has resulted from the scraping to start the reaction and that the heat of reaction has spread the glow over the entire surface.

Experiment 2.—Finding it difficult to prove the existence of a film of moisture by attempting to remove it mechanically,

a second experiment was performed in which pure oxygen dried with phosphorus pentoxide was brought in contact with pure phosphorus, the surface of which was uncontaminated. The purpose of this experiment was to determine whether or not reaction proceeded in a case where a film of moisture or oxide was impossible at the start.

A tube of about 12 mm diameter was sealed at one end and drawn out near the closed end so that a bulb was formed of about 3 cc capacity. Phosphorus and phosphorus pentoxide were placed in the tube which was then evacuated and sealed off while the phosphorus was melted, thus excluding all but phosphorus vapor. Phosphorus was then distilled into the bulb, which was sealed and cut off. Thus the phosphorus was pure, dry, and its surface perfectly clean.

The bulb of phosphorus was then placed in a desiccator containing phosphorus pentoxide and filled with oxygen thoroughly dried with phosphorus pentoxide. The desiccator was cooled to 10° in a refrigerator and the pressure regulated to 760 mm. After standing for some time at 10° the bulb of phosphorus was broken by means of a metal rod inserted in a rubber stopper in the tubulure in the top of the desiccator. The oxidation was very rapid indeed and a bright light was emitted.

Experiment 3.—The result of the preceding experiment would seem to indicate that at 10° pure, dry phosphorus will burn in dry oxygen at atmospheric pressure. To test this further another experiment was performed somewhat similar to the foregoing. Two bulbs containing phosphorus were prepared, one containing the element dried as in Experiment 2; and a second prepared in the same way without drying the element with phosphorus pentoxide. These two bulbs were placed in dried oxygen at 10° and 760 mm. The bulb containing moisture was broken first. A little flash of light appeared showing that the phosphorus vapor had ignited, but the mass of the phosphorus did not oxidize. The second bulb was then broken and a violent oxidation took place exactly as in Experiment 2.

There are two possible explanations of the results of the two preceding experiments: First, we may assume that a protecting film is formed by the water present in the bulb containing moisture; and that this film prevented the ignition of the mass of the phosphorus from the glowing vapors; or, second, that the amount of phosphorus vapor in the bulb containing moisture was insufficient to cause a rise in temperature sufficiently great to ignite the mass. Since the wet and the dry bulbs were evacuated to the same pressure before sealing, it is evident that there is less phosphorus vapor in the one containing moisture on account of the partial pressure of the water vapor When the bulb was broken, the phosphorus vapor ignites. If the burning of the vapor in the dry bulb raises the temperature sufficiently high to ignite the mass of the phosphorus, we may say that the combustion of the smaller amount of vapor in the bulb containing moisture is insufficient to raise the temperature at the surface of the mass to the ignition temperature.

If we accept the first explanation, water vapor is the protecting substance and we might expect a piece of phosphorus that is pure and dry to react with oxygen at any pressure; if we accept the second, we should not have oxidation at high pressures unless the temperature were sufficiently high

The next point to be determined is whether phosphorus pure and dry does react with dry oxygen at atmospheric pressure when precautions are taken to exclude phosphorus vapor at the outset and to avoid a gradual rise in pressure from the vapor pressure of phosphorus to 760 mm. Jorissen and Ringer[1] observed a slight oxidation at the beginning of their experiments with phosphorus and oxygen at atmospheric pressure dried by phosphorus pentoxide. This initial action was probably the oxidation of the vapors since it lasted but a short time. If the pressure is allowed to rise from the vapor pressure of phosphorus to atmospheric pressure, it is evident that at some point a pressure is attained which corresponds to the maximum reaction velocity. This period,

[1] Loc. cit.

however short, will affect the temperature at the surface of the phosphorus and so should be avoided. This was accomplished as described in the subsequent experiment.

Experiment 4.—Since it has been found that the pressure above which no reaction takes place increases with increasing temperature and since it was desired to carry out the experiment at atmospheric pressure, it was important to work at a temperature such that 760 mm would be well above the boundary pressure, if such exists. The temperature chosen was 5°. It was obviously necessary to avoid fluctuations in temperature throughout the entire experiment and to arrange to detect the slightest evidence of reaction. This was accomplished by an apparatus especially constructed for the purpose. A diagram of this apparatus is shown in Fig. I.

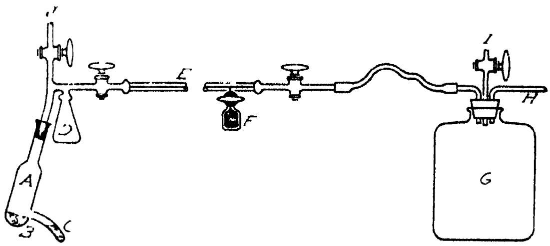

Fig. 1

The reaction vessel *A* is fitted to the manometer by a ground glass joint. *B* is a bulb containing phosphorus pentoxide. *E* is a horizontal capillary tube into which a short thread of mercury may be introduced at *F* by opening the stopcock and compressing the bulb containing mercury. The end of the manometer *E* connects by flexible pressure tubing with an eight liter bottle *G*, to which is also connected a mercury manometer *H* and an inlet tube *I*. Tube *A* and manometer *E* were clamped rigidly to an iron frame so that the whole may be rotated to bring tube *A* into a vertical position.

The procedure was as follows: Tube *A* was first removed and clamped in a vertical position. Freshly distilled white phosphorus was melted under water and run into *B* until the level was flush with the edge of the side tube *C*. The tube

was next cooled in ice water until the phosphorus solidified. When at approximately 10° the water was poured off and purified, redistilled mercury introduced into the side tube *C*. The tube *A* was immediately connected to *E*, clamped in a vertical position and evacuated by a pump at *J*, the stopcock at the end of *E* being closed. While evacuation was proceeding *A* was immersed in a water bath at 75°, thus distilling out any moisture and filling the apparatus with phosphorus vapor. After a time the evacuation was stopped and all stopcocks closed and sealed with wax. The tube *A* was kept immersed in water at 75° and the whole was allowed to stand for 72 hours to dry. Since phosphorus pentoxide was present in large excess, the inside of the apparatus may be considered thoroughly dry. While being dried, the phosphorus was in the molten state so that a fresh surface was continually being formed.

When drying was complete, *A* was cooled to 5°. The frame was set so that *E* was horizontal and *A* rotated until the mercury flowed over the surface of the phosphorus. Oxygen was then admitted from *G* and the entire apparatus swept out by a stream of oxygen thoroughly dried by passing through a series of towers filled with phosphorus pentoxide. At this point, the barometer was read and the pressure in *G* regulated to exactly 760 mm, *A* being held at 5°. The stopcocks at *J* and *I* were then closed and a thread of mercury introduced at *E*. Since *A* had a volume of about 50 cc and *E* was approximately 1 mm in cross section, observation of change in volume amounting to 1 part in 25,000 was possible.

To expose the phosphorus all that was necessary was to rotate the tube *A* until the mercury flowed back into side tube *C*. In this way there was no gradual change of pressure from the partial pressure of phosphorus to 760 mm and so the temperature at the surface of the phosphorus could be accurately known. At 5° and 760 mm there was no change in volume detected even after standing four hours. Action could be started, however, either by lowering the partial pressure of the oxygen or by raising the temperature.

In the light of this and the preceding experiments we conclude that solid phosphorus, however pure and dry, will not react with oxygen under pressures which exceed a certain value called the boundary pressure. The results are in accord with those of Jorissen.

Let us next consider three simple experiments in connection with a theory for explaining the phenomena.

Experiment 5.—A tube about 50 cm in length with a stopcock at one end and containing a bit of phosphorus, was evacuated while the phosphorus was being heated so that the tube was filled with the vapors of phosphorus. If now oxygen is admitted at the stopcock, a glow will start at that end and advance along the tube at a rate depending on the rate of entrance of the oxygen, its rate of diffusion, the partial pressure of the phosphorus and the rate of diffusion of the phosphorus vapor.

Experiment 6.—A small piece of phosphorus was placed in a tube opened at both ends. As the phosphorus slowly oxidized in the air, it showed its characteristic luminescence. If now a current of air at the same temperature of that in the tube is passed over the bit of phosphorus the glow instead of increasing will diminish and if the current of air is sufficiently rapid, the glow will disappear entirely.

Experiment 7.—In order to show that there is very little, if any, phosphorus vapor present when phosphorus is exposed to pure oxygen at atmospheric pressure and below 27°, the following experiment was carried out: Two glass bulbs, one of 50 cc and the other of 100 cc capacity were connected by a 3 mm stopcock. In the smaller bulb was placed a lump of moist phosphorus after which the apparatus was washed with a stream of oxygen. It was next placed in a refrigerator held between 15° and 20° for more than twenty-four hours with the stopcock between the bulbs open, in order to allow diffusion of any phosphorus vapors that might be present. The stopcock was then closed and the pressure in the larger bulb reduced slowly while observing carefully in a dark room. No luminescence whatsoever was obtained. Since the pres-

ence of an extremely minute trace of phosphorus can be detected in this way,[1] its absence has been proven under the conditions of the experiment.

The experiment above described was repeated, using phosphorus and oxygen that were thoroughly dried by phosphorus pentoxide. Similar results were obtained.

Discussion of Results

Since it is altogether probable that the reaction between phosphorus and oxygen takes place in the vapor phase, the velocity of the reaction, V, is proportional to the product of the concentration of the phosphorus, C_p, raised to the power x and the concentration of the oxygen, C_o, raised to the power y. Thus:

$$V = k\, C_p^x \cdot C_o^y.$$

Now it is usual to assume that the concentration of phosphorus vapor is constant in the presence of solid phosphorus so that the velocity will be proportional to some power of the oxygen concentration:

$$V = k_1\, C_o^y.$$

As has been pointed out, this expression holds fairly well over a limited range of pressure after correcting for the difference in rate of evaporation of phosphorus at the different pressures. Above a certain pressure, however, it does not hold. A logical explanation for this behavior is that something has interfered in some way with the rate of evaporation of phosphorus; or, in other words, that C_p^x in equation (1) is constant under given conditions only over a limited range.

When the vapors only of phosphorus are brought in contact with oxygen we may expect the reaction to proceed at a velocity proportional to the concentration of the reacting gases as formulated above. If solid phosphorus is present as a second phase, the rate of its evaporation will determine the distance from its surface at which the reaction will

[1] Schrötter: Loc. cit.; Centnerszwer: Zeit. phys. Chem., **26**, 9 (1898).

proceed. From the results of Experiment 5 above, it was pointed out that the rate of oxidation of phosphorus vapor in a tube in contact with solid phosphorus depends on the rate of entrance of oxygen, its rate of diffusion; the rate of evaporation of phosphorus and its rate of diffusion. Let us suppose that the oxygen pressure reaches a value great enough to force the reaction toward the solid phosphorus; in other words, the vapors react faster than they are formed. Under these conditions, the oxidation with production of oxides will move along the tube until the reaction takes place very close to the surface of the solid,[1] to distances where molecular attraction and adsorption are large. Under these circumstances the surface must necessarily become coated with a film of oxides. Although the thickness of this film may be of molecular dimension, phosphorus vapors will escape through it with difficulty; and any which diffuse through the film will be oxidized at such minute distances from the film that it will serve only to thicken the protection. Hence as long as the partial pressure of oxygen remains above a certain value the velocity of oxidation will be negligibly small. Now if in any way the partial pressure of the oxygen is diminished or the rate of evaporation of phosphorus becomes larger, the film will be broken down and oxidation will begin near the surface and proceed away from it, followed by a cloud of oxide particles. When the temperature at the surface is raised sufficiently by the heat of the reaction near it, the reaction proceeds violently.

From the standpoint of the above theory, it is possible to explain many of the apparent peculiarities in the behavior of phosporus in oxygen. First of all, it furnishes a picture of conditions at the so-called boundary pressure and explains the cause of the variability under different conditions. Whenever the partial pressure of the oxygen exceeds a certain pressure—the boundary pressure—at a given temperature, the oxidation is forced so close to the surface that a protecting film of oxide is formed which prevents further vaporiza-

[1] Cf. Ewan: Loc. cit.

tion and oxidation. Increasing the temperature at the surface of the phosphorus by the addition of external heat, by friction or by speeding up the oxidation catalytically with a trace of moisture or ozone, will increase the rate of evaporation and hence the boundary pressure is greater the higher the temperature and *vice versa.* In general, any factor which diminishes oxygen concentration or rate of diffusion or increases phosphorus vapor pressure or rate of diffusion will increase the boundary pressure and *vice versa.*

It will be recalled that the boundary pressure was quite well defined with the same piece of phosphorus and the same oxygen providing the same procedure was followed in the determination. However, the boundary pressure varies widely under different conditions and different methods of experimental procedure. Considering the above mentioned factors that determine the boundary pressure, it is not surprising that the value is not constant.

The theory above given explains Centnerszwer's observation that the pressure necessary to produce luminescence is not sharply defined; but depends on whether this pressure is approached slowly or suddenly. Attention has been called to the probability that the glow pressure is somewhat lower than the real boundary pressure, since a glow is obtained only when a reaction reaches a certain critical velocity.[1] From the standpoint of the theory, the glow pressure is the point at which the pressure of the phosphorus vapor breaks down the protecting film and reacts sufficiently rapidly to cause a continuous luminescence. From this point of view it is quite likely that if the pressure is reduced very slowly indeed, the film will break down under the prolonged pressure of the phosphorus vapor at a point as much as 50 mm higher than if the evacuation to the approximate glow pressure is made in a few seconds. Moreover, it is quite probable that the intermittent luminescence observed by Centnerszwer in the critical region between the so-called boundary pressure

[1] Bancroft: Jour. Franklin Inst., **175**, 129 (1913).

and glow pressure is due to the periodic breaking down and reformation of the protecting oxide film.

The effect of catalytic agents such as moisture, ozone, etc., on the velocity of the oxidation and hence on the boundary pressure will be considered in a subsequent communication.

The point of view above outlined emphasizes the importance of the partial pressure of oxygen and so explains why the same piece of phosphorus will glow in air and not in oxygen at the same temperature and pressure. It also explains the parallel case described in Experiment 6, that the luminescence of phosphorus may be put out or "blown off" the surface by a current of air. Circulating air has the same effect as increasing the oxyen concentration or of increasing the pressure of the same mixture.

The importance of the combined influence of temperature and the partial pressure of oxygen on the rate of evaporation of an oxidizable solid and hence on the location and amount of flame is brought out in the case of the oxidation of phosphorous oxide. The observations of Thorpe and Tutton[1] are so interesting in this connection that their description of the phenomena are quoted:

"Phosphorous oxide spontaneously oxidizes to phosphorus pentoxide on exposure to air or to oxygen. A small quantity of the oxide in a test-tube in contact with the air soon becomes surrounded by a voluminous deposit of the pentoxide, which deliquesces at the margin nearest the mouth of the tube. When a few decigrams of phosphorous oxide are placed at the bottom of a wide tube closed at one end, and previously filled with dry oxygen, and the tube sealed and kept in the dark, in an upright position, a bulky, snow-like deposit of pure phosphoric oxide is formed in rhythmic striae or annuli along the walls of the tube, showing that vaporization of the phosphorous oxide precedes its oxidation. The action is comparatively slow at first, but seems to proceed at an accelerated rate as the tension of the included oxygen diminishes, whereby the

[1] Jour. Chem. Soc., 57, 569 (1890); cf. L. and E. Bloch: Comptes rendus, 147, 842 (1908)

volatility of the phosphorous oxide is increased. Under diminished pressure, the tube is seen to be more or less filled with a luminous fluctuating glow, which instantly stops when the tension is increased to atmospheric pressure By increase of temperature, effected by warming the outside of the tube with a water-jacket, the diminution of pressure required to produce the glow becomes less—a further proof that the glow is due to the action of oxygen on the *vapor* of phosphorous oxide. If the temperature is gradually raised to about 70°, the rate of volatilization, and consequent oxidation, is such that the mass of phosphorous oxide burns, but the vigorous combustion can be at once stopped by reducing the pressure of the oxygen, and immediately renewed by restoring the pressure, and the experiment can be repeated until the whole of the oxide or the oxygen is used up.

"The change from glow to actual flame is perfectly regular and gradual, and is unattended with any sudden increase in brilliancy. In this respect, the process of oxidation is analogous to the slow and barely visible burning of fire-damp which is sometimes seen to occur in the Davy lamp. * * "

As in the case of phosphorus, the flame approaches close to the surface with high pressure of oxygen at 20°; and at 760 mm the flame disappears. The disappearance of flame does not mark a boundary pressure, however, since the oxidation does not cease entirely under these conditions, as in the case of phosphorus. This is due to the fact that the formation of a coherent protecting film of pentoxide is prevented on account of the much higher vapor pressure of phosphorous oxide than of phosphorus under the same conditions.

Summary

(1) When the vapors only of phosphorus are brought in contact with oxygen, the reaction proceeds at a velocity proportional to the concentration of the reacting substances: $V = k\, C_p^x \cdot C_o^y$. It is usually assumed that the concentration of phosphorus vapor is constant in contact with solid phosphorus and hence that the velocity of oxidation is pro-

portional to the concentration of oxygen: $V = k_1 C_o^y$. This is not the case below 25° and above a certain partial pressure of oxygen—the boundary pressure—owing to the formation of an oxide film on the surface of the phosphorus.

(2) The conditions necessary for the formation of a protecting film are as follows: The rate of oxidation of phosphorus vapor in a tube in contact with solid phosphorus depends on the rate of entrance of oxygen, its rate of diffusion; the rate of evaporation of phosphorus and the rate of diffusion of phosphorus vapor. If the oxygen pressure is great enough to force the reaction toward the solid phosphorus, the oxidation will move along the tube until the reaction takes place very close to the surface of the phosphorus, to distances where molecular attraction and adsorption are large. Under these conditions the surface will become coated with a film of oxide. Although the thickness of this film may be of molecular dimension, phosphorus vapor will diffuse through it with difficulty; and any which diffuses through will be oxidized at such minute distances from the film that it will serve only to thicken the protection.

(3) The protecting film will be destroyed by decreasing the partial pressure of oxygen below a certain value or by increasing the rate of evaporation of phosphorus. Under these conditions, oxidation will begin near the surface of the phosphorus and proceed away from it.

(4) The boundary pressure is the partial pressure of oxygen above which a protecting oxide film prevents the vaporization and oxidation of phosphorus. It is not constant since any factor which diminishes oxygen concentration or rate of diffusion or increases phosphorus vapor pressure or rate of diffusion will increase the boundary pressure and *vice versa.*

(5) It is quite probable that the intermittent luminescence observed by Centnerszwer in the narrow critical region between the so-called boundary pressure and glow pressure is due to the periodic breaking down and reformation of the protecting oxide film.

(6) The luminescence of a piece of phosphorus in air may

be put out or "blown off" the surface by a current of air. Circulating air has the same effect as increasing the oxygen concentration or of increasing the pressure of the same mixture.

Investigations are being continued on the emissions from glowing phosphorus and on the nature of the so-called catalytic action of certain vapors on the oxidation of phosphorus.

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NEW BOOKS

The Nature of Animal Light. *By E. Newton Harvey. 21 × 14 cm; pp. x + 182. Philadelphia: J. B. Lippincott Company, 1920. Price: $2.50.*— In this extremely interesting book the subject is presented under the following headings: light-producing organisms; luminescence and incandescence; physical nature of animal light; structure of luminous organs; the chemistry of light production; dynamics of luminescence. A good general idea of the scope and style of the book can be obtained from the following quotations, pp. 11, 14, 41, 78, 89, 103, 140, 149, 153.

"Apparently there is no rhyme or reason in the distribution of luminescence throughout the plant or animal kingdom. It is as if the various groups had been written on a blackboard and a handful of sand cast over the names. Where each grain of sand strikes, a luminous species appears. The *Coelenterates* have received most sand. Luminescence is more widespread in this phylum and more characteristic of the group as a whole than any other. Among the arthropods luminous forms crop up here and there in widely unrelated groups. In the mollusks, excluding the cephalopods, only two luminous species are known. Several *phyla* contain no luminous forms whatever. It is an extraordinary fact that one species in a genus may be luminous and another closely allied species contain no trace of luminosity. There seems to have been no development of luminosity along direct evolutionary lines, although a more or less definite series of gradations with increasing structural complexity may be traced out among the forms with highly developed luminous organs."

"Apart from these cases where light is actually produced but is not primary, not produced by the animal itself, there are many forms whose surface is so constituted as to produce interference colors. This is true in many cases among the birds and butterflies whose feathers and scales are iridescent. Some of these have been erroneously described as luminous. Perhaps the best known case among aquatic animals is *Sapphirina,* a marine copepod living at the surface of the sea, and especially likely to be collected with other luminous forms. Its cuticle is so ruled with fine lines as to diffract the light and flash on moving much as a fire opal. Needless to say no trace of light is given off from this animal in a totally dark room.

"It has often been supposed that the eye of a cat or of other animals is luminous. The eyes of a moth, also, can be seen to glow like beads of fire when it is flying about a flame. Both of these cases are, however, purely reflection phenomena and due to reflection out of the eye again of light which has entered from some external source. The correct explanation was given by Prevost in 1810. The eye of any animal is quite invisible in absolute darkness. The same explanation applies to the moss, *Schistostega,* which lives in dimly illuminated places and whose cells are almost spherical, constructed like a lens, so as to refract the light and condense it on the chloroplasts at the bottom of the cells. Some of this light is reflected out of the cells again and gives the appearance of self-luminosity. The alga, *Chromophyton rosanoffii,* is another example of apparent luminosity, due to reflection from almost spherical cells."

"It is a fact that different luminous animals produce light of quite different

colors as judged by our eye. A range of spectral tints has been described which extends from red to violet but 'yellowish,' 'greenish' and 'bluish' tints are commonest. Indeed one or two animals possess several luminous organs emitting lights of different colors. This is true in a South American firefly, *Phengodes*, whose lights are red and greenish yellow, and in the deep sea squid, *Thaumatolampas diadema*, which produces lights of three colors, two shades of blue and red. The red light in the case of the squid appears to be due to a red color screen formed by the chromatophores, but in *Phengodes* no screen is present.

"Curiously enough, the light organ of the larva of the firefly (glowworm) is quite distinct from that of the adult. Like so many other structures in insects, the adult organ is developed anew from potential photogenic cells during the pupal period. Even the egg of the firefly is luminous and glows with a steady light, and during the pupal period light may sometimes be seen coming from the thoracic region.

"In the firefly there is no true lens, the light merely shining through the cuticle which is transparent over the light organ, whereas over the rest of the body it is dark and pigmented. In the deep sea shrimp, *Acanthephyra debelis*, with light organs scattered over the surface of the body, the cuticle covering the light organ forms a concavo-convex lens, behind which are the photogenic cells (Kemp, 1910). The lens is made up of three layers which suggest that it may be corrected for chromatic aberration—a veritable 'achromatic triplet.' In an allied form, *Sergestes*, the lens is of two layers and double convex. Optical studies of these lanterns have been made by Trojan (1907). The lens of these organs is also bluish in color which suggests that they may serve also as color filters. Behind the photogenic cells is a mass of connective tissues through which enters the nerve, for the light of these organs is under the control of the animal and may be flashed at will."

"It should be clearly borne in mind that if we place luminous organisms, say bacteria or fungi, in an atmosphere devoid of oxygen and find that no light is produced, this may merely mean that certain functions of the cell are interfered with, including light production, but does not necessarily indicate that oxygen is actually used up in the photogenic process. If we find, however, that extracts of luminous cells or luminous secretions devoid of cells cease to light when the oxygen is removed and again luminesce when it is returned, we may be quite certain that the photogenic process itself requires free oxygen. As luminous extracts of fireflies, pennatulids, ostracods, *Pholas* and others give off no light when the oxygen is removed, we may safely conclude that for these luminescences, oxygen is necessary. Bacteria, fungi, and *Noctiluca*, whose light also disappears in absence of oxygen, although they are whole cells, we may by analogy also assume to require oxygen in the photogenic process.

"Some of the earlier workers on fireflies and *Noctiluca* obtained light even after placing these organisms in absence of oxygen, but they did not realize how low is the amount of oxygen necessary to produce light. It is difficult to remove traces of oxygen from the water, traces which are nevertheless sufficient to cause luminescence. If the organisms are numerous, as in an emulsion of luminous bacteria, they will themselves use up all the oxygen and the liquid soon ceases to glow except at the surface in contact with air. We may gain an idea of the amount of oxygen necessary for luminescence from an experiment of

Beijerinck (1902). He mixed luminous bacteria with an emulsion of clover leaves containing chloroplasts and kept the two in the dark until all the oxygen was used up and the bacteria ceased to glow. If now a match was struck for a fraction of a second, sufficient oxygen was formed by photosynthesis to cause the bacteria to luminesce for a short time.

"Exact figures on the minimal concentration of oxygen for luminescence cannot be given. The luminescent secretion of *Cypridina hilgendorfii* will still give off much light if hydrogen containing only 0.4 percent of the oxygen is bubbled through it, i e., a partial oxygen pressure of 1/250 atmosphere (3.04 mm Hg). However, addition of a fresh emulsion of yeast cells to a glowing *Cypridina* secretion is sufficient to rapidly extinguish the light, because the yeast is capable of utilizing the last trace of oxygen in the mixture. Light only appears when, by agitation, we cause more air to dissolve. The mineral concentration of oxygen for luminescence of *Cypridina* lies somewhere between 3.04 mm and the amount which living yeast fails to extract from solution, a concentration approaching zero. It is probably nearer the latter figure.

"As the oxygen pressure is increased from 0 to about 7 mm, the intensity of the *Cypridina* luminescence increases and at the latter figure the light is just as bright as if the solution were saturated with air (152 mm O_2). Thus, the luminescence requires only a low pressure of oxygen and the similarity to the saturation of haemoglobin with oxygen is obvious. Just as haemoglobin is nearly saturated with oxygen at low pressures and becomes bright red in color, so the luminous material becomes saturated with oxygen at low pressures and glows intensely."

"A very great advance in our knowledge of the chemistry of the problem was made by Dubois in 1885. He showed that if one dips the luminous organ of *Pyrophorus* in hot water, the light disappears and will not return again. Also if one grinds up a luminous organ the mass will glow for some time but the light soon disappears. If one brings the previously heated organ in contact with the unheated triturated organ it will again give off light. Later, Dubois showed that the same experiment could be peformed with the luminous tissues of *Pholas dactylus*. A hot-water extract of the luminous tissue, and a cold-water extract of the luminous tissue, allowed to stand until the light disappears, will again produce light if mixed together. Dubois (1887) advanced the theory that in the hot-water extract there is a substance, luciferin, not destroyed by heating, which oxidizes with light production in the presence of an enzyme, luciferase, which is destroyed on heating. The luciferase is present together with luciferin in the cold-water extract, but the luciferin is soon oxidized and luciferase alone remains. Mixing a solution of luciferin and luciferase always results in light production until the luciferin is again oxidized. Similar substances have been found by me in the American fireflies, *Photinus* and *Photuris*, the Japanese firefly, *Luciola*, and in the ostracod crustacean, *Cypridina hilgendorfii*. Crozier reports that they exist also in *Ptychodera*, a balanoglossid. I have been unable to demonstrate their existence in luminous bacteria; in the annelid, *Chaetopterus;* the pennatulids, *Cavernularia* and *Pennatula;* the squid, *Watasenia;* and the fish, *Monocentris japonica*. E. B. Harvey (1917) could not demonstrate them in *Noctiluca*. There are several reasons why the existence of such bodies might be difficult to demonstrate, but these reasons cannot be considered here. We

thus see that the photogen is in reality of dual nature, that two substances are necessary for light production and that they may be very readily separated because of difference in resistance to heating. In this respect Bioluminescence is similar to some other biological processes, notably to certain immune reactions and to certain enzyme actions."

"In summing up we may say that the luminescence of at least three groups of luminous animals, the beetles, *Pholas*, and *Cypridina*, has been definitely shown to be due to the interaction of two substances, luciferin and luciferase, in presence of water and oxygen. Luciferin and luciferase have quite different properties and may be easily separated from each other by various chemical procedures. As the luciferins and luciferases from different luminous animals have somewhat different properties, they may be designated by prefixing the generic name of the animal from which they are obtained.

"*Cypridina* luciferin differs from *Pholas* luciferin in that it can not be oxidized with light production by $KMnO_4$, H_2O_2, with or without haemoglobin, or similar oxidizing agents. *Cypridina* luciferase differs from *Pholas* and firefly luciferase in that it is not readily destroyed by the fat-solvent anaesthetics, such as chloroform, ether, etc. When *Cypridina* luciferin is oxidized, no fundamental splitting of the molecule occurs, because the product, oxyluciferin, can be readily reduced to luciferin again. This reduction is brought about under conditions similar to those necessary for the reduction of dyes, such as methylene blue. Oxyluciferin can be reduced to lúciferin, which will again give light with luciferase, by the reductases of muscle tissue, liver, etc., or by bacteria; by Schardinger's enzyme of milk; by H_2S; by the nascent hydrogen from the action of acetic acid on magnesium or of water or NaOH on aluminum, zinc or magnesium; and by palladium black and sodium hypophosphite, all well-known reducing methods. Reduction of oxyluciferin no doubt occurs even in presence of luciferase if oxygen is absent, and reduction of oxyluciferin no doubt occurs in animals which burn luciferin within the cell, thus tending for conservation of material. Dilute alkali favors oxidation and dilute acid favors the reduction. Light favors the reduction of oxyluciferin.

"Apparently luciferin and oxyluciferin have identioal chemical properties. Neither is digested by the enzymes: malt diastase, ptyalin, yeast invertase, pepsin, trypsin, steapsin, amylopsin, rennin, erepsin, urease or enzymes occurring in the water extracts of dried spleen, kidney, or liver. Luciferase is destroyed only by pepsin (probably), trypsin, erepsin, in spleen and liver extract.

"Luciferase is unquestionably a protein and all its properties agree with those of the albumins. Although used up in oxidizing large quantities of luciferin, it behaves in many ways like an enzyme and may be so regarded. Luciferin, on the other hand, is not digested by proteolytic enzymes, is dialyzable, almost but not completely precipitated by saturation with $(NH_4)_2SO_4$, and is soluble in absolute alcohol, and some other organic solvents, but not in the strictly fat-solvents like ether, chloroform, and benzol. There are, however, certain CO-NH linkages which are not attacked by proteolytic enzymes and some peptones soluble in absolute alcohol, so that these two characteristics do not bar it from the group of proteins. Luciferin, in fact, has many properties in common with the proteoses and peptones but its chemical nature cannot be definitely stated at present."

"It should be noted that the intensity of luminescence of pyrogallol oxidized with most oxidizers is actually less at the boiling point, a fact which I have repeatedly verified. Let us now see how these facts are to be explained. If we assume that luminescence is dependent on reaction velocity, the intensity of luminescence should increase with increasing temperature. Up to a certain limit this is what we find, but at temperatures above this limit the intensity of luminescence actually decreases. The duration of luminescence also decreases. There is an optimum temperature for luminescence in many cases and we can only conclude that luminescence depends not on a very rapid reaction velocity but on a certain definite reaction velocity. Assuming that this is true, how can we account for the anomalous fact that in high concentrations of oxygen, phosphorus will not luminesce or that in high concentrations of pyrogallol, there is no luminescence in presence of ozone or of oxidizer and H_2O_2. Of course with high active mass of oxygen (in case of phosphorus luminescence) or of pyrogallol (in case of pyrogallol luminescence) the reaction velocity must be greater than the optimum. If that is the case, then lowering the temperature should reduce the reaction velocity to the optimum and light should appear. However, as we have seen, not lowering but raising the temperature causes luminescence with high oxygen concentration or high pyrogallol concentration.

"I believe the explanation of these phenomena lies rather in another direction and that the effect of the temperature and concentration of reacting substances affects not only the reaction velocity but also the reaction products. While intensity of luminescence undoubtedly increases with increasing reaction velocity, the luminescence itself probably accompanies only one stage in the formation of a series of oxidation products. This stage is favored at a definite temperature and mass of reacting substances. Thus, in the oxidation of phosphorus several intermediate oxides are said to be formed. The oxidation takes place in steps and probably the luminescence is connected with only one of the steps in a chain of reactions. It is probable that a certain oxygen pressure and temperature favors that particular step at the expense of the others and so this oxygen concentration and temperature correspond to the optimum for luminescence.

"The supposition that certain definite oxidation products of pyrogallol must be formed in order to produce light is borne out by the fact that pyrogallol must be oxidized in a particular way to obtain luminescence. The blackening of pyrogallol with absorption of oxygen in presence of alkali is a very well-known reaction, but luminescence does not accompany this type of oxidation. I have tried mixing all concentrations of pyrogallol and all concentrations of alkali in an endeavor to obtain some light, but always with negative results. Likewise my attempts to obtain light during the electrolysis of salt solutions containing pyrogallol by means of the nascent oxygen of various kinds of anodes have met with negative results. A similar case is presented by luciferin which oxidizes spontaneously (most rapidly in presence of alkali) without light production and only produces light when oxidized in presence of luciferase.

"To sum up the results of the dynamics of chemiluminescence we may say that certain oxyluminescences occur only if the substance is oxidized in a particular way under definite conditions of temperature and concentration and that this is probably due to a favoring of one step (with which the luminescence is associated) in a chain of oxidations. Providing temperature and con-

centration are such as to favor the step responsible for luminescence, then higher temperature and greater concentration result in increased intensity of luminescence."

This is exactly the kind of monograph that is wanted—a book on an interesting subject written by the expert. In a second edition it would be well to change the abnormal spelling of desiccators and a few other words, which the proof-reader overlooked.

The Determination of Hydrogen Ions. *By W. Mansfield Clark. 23 × 16 cm; pp. 317. Baltimore: Williams and Wilkins Company, 1920. Price: $5.00.* —There are many people who have to determine hydrogen ion concentrations for one reason or another, and it means a great saving to them if they can find all the details of such determinations brought together in one book. There is, therefore, a very great need for a book of the sort that Mr. Clark has written. He puts it rather modestly. "It is not because the author feels especially qualified to make such an exposition that this book is written; but rather because, after waiting in vain for such a book to appear, he has responded sympathetically to appeals, knowing full well from his own experience how widely scattered is the information under daily requisition by scores of fellow workers "

The titles of the chapters are: introduction; outline of the chief colorimetric procedure; theory of indicators, choice of indicators; standard buffer solutions for colorimetric comparisons; the protein and the salt errors in colorimetric determinations; approximate determinations with indicators; outline of the electrometric method; theory of the hydrogen electrode; potential differences at liquid junctions; hydrogen and calomel electrodes and electrode vessels; the potentiometer and accessory equipment; hydrogen generators, wiring, shielding, temperature control, purification of mercury; the relation of hydrogen electrode potentials to reduction potentials; sources of error in electrometric measurement of pH; standard solutions for checking hydrogen electrode measurements; standardization of pH measurements; supplementary methods; applications; bibliography; appendix.

In regard to protein errors, the author says, p. 84: "If there are present in a tested solution bodies which remove the indicator or its ions from the field of action either by absorption or otherwise, the equilibria which have formed the basis of our treatment will be disturbed. An indicator in such a solution may show a color intensity, or even a quality of color, which is different from that of the same concentration of the indicator in a solution of the same hydrogen ion concentration where no such disturbance occurs. We could easily be led to attribute very different hydrogen ion concentrations to the two solutions. This situation is not so uncommon when we are dealing with protein solutions, for, in some instances, there is distinctly evident the removal of the indicator from the field."

On p. 185 it is stated that "there are effects of unknown cause which are included under the term 'poisoned electrodes.' An electrode may be 'poisoned' by a well-defined cause such as those to be mentioned presently; but occasionally an electrode will begin to fail for reasons which cannot be traced. There is hardly any way of putting an observer on his guard against this except to call his attention to the fact that, if he is familiar with his galvanometer, he will notice a peculiar drift when balancing his E. M. F.'s. Arsenic deposits, adsorption

of material by the platinum black (with such avidity sometimes that redeposition of the black is necessary), the deposit of films of protein have all been detected as definite causes of electrode poisoning. Michaelis (1914) places free ammonia and hydrogen sulphide among the poisons."

On p. 35 we are told that "the maintenance of neutrality by such solid reagents as calcium carbonate may be considered as a buffer action. It is very important to note however that the use of calcium carbonate may become a grossly inefficient procedure. To show its inefficiency the author has placed at the bottom of a test-tube a deep layer of very finely divided, freshly precipitated and well washed calcium carbonate and overlaid this with cultures of bacteria and molds in sugar media. Indicators show that, unless the calcium carbonate is frequently and thoroughly shaken with the medium, only the solution in direct contact with the calcium carbonate is neutralized. Molds may be develop an acidity as high as pH2 within a few millimeters of the carbonate."

On p. 65 are given the indicators recommended by the author. They are all phthaleines and with one exception sulfone phthaleines. Since most of these involve a change from yellow to something else, it might have been well to point out that the use of a suitable yellow glass would make the end point very much sharper.

The book is a good one and will prove very useful to many people. The author has not always remembered that his readers are not as familiar with the subject as he is. On p. 113 he gives the absolute velocity of hydrogen ion as 32.5×10^{-4} cm/sec at 18° and its mobility as 318.0; but there is nothing to show under what conditions the hydrogen ion has this velocity or what the relation is between it and the mobility. On p. 184 the author says that "there is hardly any use attempting the measurement of unbuffered solutions, if indeed there would be any significance to the measurement were it accurate;" but he does not tell us how to buffer a solution when its pH is unknown. On p. 212 the diagram for the titration of hydrochloric, acetic and boric acids in presence of methyl red or phenolphthalein would be much clearer if the diagram had been extended sideways so as to show what would happen with a drop or two of caustic soda in excess. This is the more desirable because we always do over-run a trifle when making titrations. On p. 148 the resistance of the voltmeter will make a difference in the potential drop unless the voltmeter circuit is kept closed all the time, which is not customary. On p. 144 it is a question whether the average reader will realize that the author meant to say that the cell is measured on open circuit. The matter of the sign of the potential is left in the air, p. 107, and it is very much of a question how much the reader will get out, p. 25, of the discussion of iso-electric points. These things are not of great importance; but they should be changed in the next edition. *Wilder D. Bancroft*

ON THE CATALYTIC HYDROGENATION OF COTTON-SEED OIL

BY LOUIS KAHLENBERG AND GEORGE J. RITTER[1]

INTRODUCTION

The purpose of this investigation is to study the catalytic process of the hydrogenation of cottonseed oil, in the hope of ascertaining the best conditions for conducting the process, and also finding new catalysts that will effectively bring about the reduction of the oil. To this end it was first necessary to make an exhaustive study of the literature of the subject. This study revealed the fact that to a large extent our knowledge of the actual process of the hydrogenation of oils is contained in the patent literature. Furthermore, in most of these patents in question, experimental details are not given sufficiently to enable one to duplicate the processes in the laboratory. It was consequently necessary to supplement the study of the literature with experimental work in the laboratory to get a proper understanding of the known processes of the hydrogenation of oils. After such study, the investigation of unknown fields could proceed.

This paper is consequently divided into the following parts:

1. Historical Study of the Literature.
2. Experimental Review of Certain Typical Known Catalytic Processes.
3. New Experimental Work.
4. Summary and Conclusions.

I. HISTORICAL REVIEW

The process of hydrogenating unsaturated oils began in 1875, when Goldschmidt[2] succeeded in reducing oleic acid by means of hydriodic acid and amorphous phosphorus at 200° C.

Wilde and Reychler,[3] in 1888, heated oleic acid at 208° C

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[1] From a thesis submitted for the degree of Ph.D. at the University of Wisconsin.

[2] Sitzungsber. Akad. Wiss. Wien, **72**, 366 (1875).

[3] Bull. Soc. chim. Paris, **1**, 295 (1889).

with one percent of iodine and a small amount of tallow soap, and then boiled the mixture with acidulated water. By distilling the product part of the iodine was recovered from the pitchy residue. They claim to have obtained approximately a seventy percent yield of stearic acid. However, thirty percent of the iodine used could not be recovered in this process.[1]

Weineck,[2] in 1886, claimed that it was possible to hydrogenate oleic acid by means of the electric current.

In a patent taken out by Magnier[3] the oil is acidified with sulphuric acid, mixed with about five times its volume of water, and then subjected to the action of an electric current under five atmospheres of pressure. The nascent hydrogen generated by the current reduces the olein to stearine.

De Hemptinne[4] reduced oleic acid to stearic acid by means of a method in which thin layers of the fatty acid were brought into the path of an electric current which passed through a chamber filled with hydrogen. His percentage yields were quite low.

Petersen[5] succeeded in reducing oleic acid to stearic acid by passing a current of electricity between nickel electrodes immersed in an alcoholic solution of stearic acid acidulated with sulphuric acid. The yield in no case ran above twenty percent.

Böhringer and Söhne[6] worked on the same principle as Petersen, but they used platinum electrodes coated with platinum black. They obtained better yields than Petersen. One would expect fairly good results in this case, because platinum black is known to be a good catalyst. The nascent hydrogen generated by the electric current in the presence of the platinum black makes an ideal condition for the reduction of the unsaturated oil.

[1] Chem. Ztg., 595 (1889).
[2] Osterr Privil., 10, 400, July 19 (1886)
[3] British patent 3,363 (1900), German patent 126,446, October 3 (1899).
[4] U. S. patent 797,112, August 15 (1905)
[5] Zeit. Elektrochemie, 11, 549 (1905).
[6] German patents 187,788, 189,332 (1906).

In 1871 Saytzeff[1] reduced nitrobenzol to aniline by passing a mixture of nitrobenzol vapors and hydrogen over platinum black. This research laid the foundation for an intensive study of hydrogenation by Sabatier and Senderens,[2] who, in 1895, began their classic researches on oils by means of nickel and other metallic catalysts. These two investigators have worked out the fundamental principles of oil hydrogenation by metallic catalysts. In 1901 they took out the German patent 139,457 for the reduction of nitrobenzol to aniline.

The German patent 141,029 was issued to Leprince and Siveke in 1902.[3] It covers the hydrogenation of oils in the liquid state by means of metallic catalysts. In the following year the English patent 1,515 was granted to Normann. A controversy in regard to alleged infringement of patent rights between this and the Leprince patent, 141,029, led to a litigation which extended over a period of several years[4]

Believing that a more intimate mixture of oil, hydrogen and catalyzer should be obtained in order to shorten the time required to reduce unsaturated organic substances with hydrogen, Bedford and Williams[5] proposed to expose the oil in the form of a fine spray to hydrogen gas in the presence of a nickel catalyst. By this treatment linseed oil was converted into a solid fat having a melting point of 53° C. Oleic acid was reduced to stearic acid with a melting point of 69° C. A diagram of the apparatus is shown in Fig. 1.

In 1910 palladium was first used as a catalyst commercially. The Vereinigte Chemische Werke[6] was granted the German patent 236,488 and in the following year the British patent 18,642 was issued wherein palladium was precipi-

[1] Jour. prakt Chemie, (2) **4**, 418 (1871)

[2] Comptes rendus, **132**, 210, 566, 1254 (1901); Ann Chim Phys, **4**, 319 488 (1905).

[3] German patent 141,029 (1902).

[4] Ellis: "Hydrogenation of Oils," p. 605 (1919).

[5] English patent 2,520 (1907).

[6] German patent 236,488, August 6 (1910); British patent 18,642 (1911).

tated upon inactive bodies, and thus used for hydrogenating oils.

Kayser,[1] in 1911, introduced the idea of hydrogenating under pressure and at the same time mechanically stirring in the oil during the reducing process. He used a nickel catalyst deposited upon "kieselguhr." This method is of interest for several "Crisco" factories in this country are using this process with slight modifications.[2] The diagram of Fig. 2 shows the important features of the apparatus used in this process.

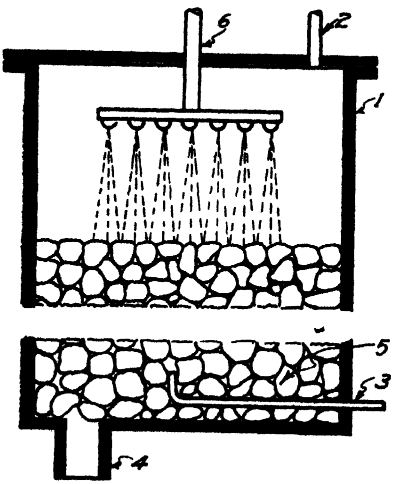

Fig. 1

The process calls for the use of hydrogen under pressure, but no specified pressure is mentioned in the patent.

Wilbuschewitch[3] was granted a patent which specified that the mixture of oil and catalyst should enter the top of the reaction chamber in an atomised condition. On descending in the flask the mixture meets an upward current of hydrogen. The partially reduced oil is then automatically pumped into the second of a series of reaction chambers, etc., until the desired product is obtained. A pressure of nine atmospheres is specified with a temperature of 160° C. By working at this low temperature it is claimed that a nice white fat is finally obtained.

Shukoff[4] originated a unique method for hydrogenating oils. He passed carbon monoxide over metallic nickel at 65° to 75° C to form nickel carbonyl. The vapors formed

[1] U. S. patent 1,004,035, September 26 (1911).
[2] Ellis: "Hydrogenation of Oils," p. 161 (1919).
[3] Swedish patent 992, May 27 (1911).
[4] German patent 241,823, January 18 (1910).

were conducted through cottonseed oil at 200° C. At this temperature the nickel carbonyl was decomposed into finely divided nickel and carbon monoxide. When a suitable amount of the nickel catalyst had been formed, the carbon monoxide current was shut off and a rapid stream of hydrogen was bubbled through the oil at 225° to 240° C. In five to six hours a fat which solidified at 40° C was obtained. The difficulty encountered in this process was that the catalyst being in such a fine state of division, settled out only after long standing.

Winner and Higgins[1] observed that a very active catalyst

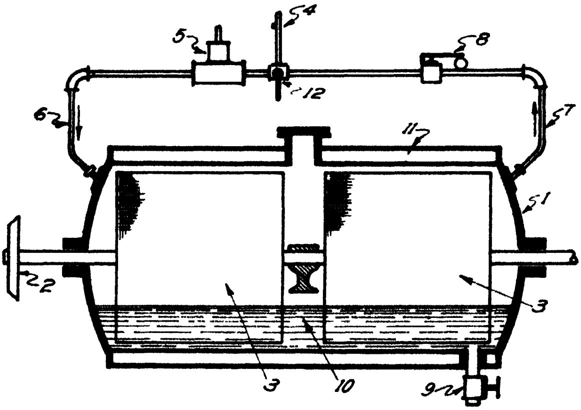

Fig. 2

could be prepared by treating nickel formate with hydrogen at 300° C. They claim that the carbon of the formate aids in reducing the nickel oxide.

In 1913 Hildescheimer[2] found that metallic boron in the presence of hydrogen would reduce cottonseed oil. He assumed that the catalytic action depends upon the intermediate formation of BH_3. High pressures and high temperatures are required. He also found that aluminium boride reduced unsaturated oils.

An American patent states that, under pressure, tungsten,

[1] French patent 454,501, February 18 (1913)
[2] Zeit. angew. Chem. Ref., 583 (1913).

molybdenum, thorium, uranium, zirconium, titanium, vanadium, and manganese may be used for hydrogenating oils.[1] Hamburger[2] contradicts this statement. He clains that the above metals can not be used in reducing oils even under 200 atmospheres.

Ellis[3] prepared an active nickel catalyst by forming an electric arc between two nickel electrodes under water.

Richardson prepared catalysts of nickel, copper, platinum, palladium, iron and their alloys by arcing electrodes of the respective metals under oil. This process gave the best catalysts when operated at pressures of 40 to 100 volts.

The Oelverwerkung G. m. b. H.[4] describes a process for manufacturing a very active catalyst by mixing nickel nitrate with sugar and reducing with hydrogen at 200° C. The catalyst in this case is in a very voluminous condition.

Rare Metal Catalyzers

Paal[5] states that platinum and palladium are good catalysts. He recommends that the chlorides of these metals be treated with sodium carbonate and the precipitate formed be added to the oil and reduced with hydrogen. Colloidal platinum for reducing unsaturated bodies was first prepared by Bredig[6] by means of the electric current in aqueous solutions of ether. Paal and Karl[7] found that palladium precipitated upon nickel, cobalt, and magnesium oxide was more active in hydrogenating oils than palladium when used alone. When palladium was deposited upon the oxide of lead, cadmium, zinc, aluminium, or iron its action was greatly diminished.

Iridium, rhodium, ruthenium, and osmium are also specified as catalyzers for unsaturated oils.[8] Lehman states that

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[1] U. S. patent 1,026,156 (1914).
[2] Chem. Weekblad., **13,** 2-13 (1916).
[3] U. S. patent 1,092,206, April 7 (1914).
[4] Italian patent 130,384, March 13 (1913); Chem. Abs., **11,** 1279 (1916).
[5] Ber. deutsch. chem. Ges., **41,** 2282 (1908).
[6] Ellis: "Hydrogenation of Oils," 245 (1919).
[7] Ber. deutsch. chem. Ges., **56,** 3069(1913); Chem. Ztg. Rep., 642 (1913).
[8] Vereinigte Chemische Werke A. G.· French patent 425,729 (1911); Seifen Ztg., **1912,** 390.

osmium dioxide is a good catalyzer. This is contradicted by Normann and Schick, who claim that it is metallic osmium which does the hydrogenating and not the dioxide.[1] Ellis[2] found that cerium incorporated with charcoal makes a very good catalyst. Mannich[3] states that platinum deposited upon charcoal is much more active than when the metal is incorporated with other inert materials, such as, silica or pumice. His view is shared by Ellis.[4] In 1916 Mittasch reported ruthenium as a catalyzer for hydrogenation processes.[5]

Mannich and Thiele[6] found that by mixing powdered, ignited, animal charcoal with a 2 percent solution of palladium chloride, and passing into this mixture a stream of hydrogen, a large volume of the gas was absorbed. The water was then evaporated and the residue dried. This catalyst was found to be very efficient in hardening oils. It has good keeping qualities; is easily filtered from the melted fat without leaving any trace of the metal in the oil. Mannich recommends this catalyst highly for hardening peanut oil.

Meyer,[7] in 1912, reported the hydrogenation of olive oil with colloidal palladium hydroxide solution which contained 0.2 grams of palladium and 0.34 grams of gum arabic per 100 cc. Two volumes of olive oil and one volume of the palladium solution were heated and stirred in an autoclave at 80° C under a pressure of 6 atmospheres Hydrogen was added to keep up the pressure; after one-half hour's treatment the oil was separated from the catalyst. A solid fat was obtained.

Ellis[8] states that in hydrogenating with palladium compounds water must be present. In this respect the palladium

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[1] Seifen Ztg., **1914,** 1111; Ellis' "Hydrogenation of Oils," 258 (1919)

[2] U. S. patent 1,167,280, January 4 (1916)

[3] Seifen Ztg., **1914,** 1174.

[4] U. S. patent 1,174,245, March 7 (1916)

[5] U. S. patent 1,173,532, February 29 (1916).

[6] Ber. deutsch. pharm. Ges., **26,** 36-38 (1916)

[7] Dissertation, Karlsruhe (1912); Ellis' "Hydrogenation of Oils," 253 (1919)

[8] "Hydrogenation of Oils," 255 (1919).

process differs from hydrogenating with most of the other catalysts. Cottonseed oil treated with colloidal palladium and hydrogen showed no reduction. No reduction took place when the reaction was conducted in alcohol or acetone, but on adding about 15 percent of water reduction took place rapidly. He states that formaldehyde and mustard oil are very "poisonous," meaning, of course, that these substances inhibit the process.

Mannich and Thiele[1] found that the capacity of palladium for adsorbing hydrogen is greatly increased by mixing animal charcoal with the metal. A catalyst for hardening unsaturated oils can readily be prepared by shaking ignited powdered animal charcoal with a two percent solution of palladium chloride, and passing hydrogen into the mixture until no more of the gas is adsorbed. The powder is then washed and dried. This catalyst has good keeping qualities.

Sulsberger[2] states that a good palladium catalyzer can be prepared by treating palladium chloride with sodium oleate. This gives a compound which readily dissolves in cottonseed oil. The oil is rapidly hardened with this catalyzer.

In reviewing the subject of the hydrogenation of oils it is noted that most of the catalysts used are found in Group 8 of the periodic table of elements. Of late years considerable experimental work has been done on some of the rare elements. Commercially, nickel and cobalt play the important rôle as catalytic agents in preparing lard substitutes. The methods of preparing these agents are many. In the arts, the preparations are trade secrets.

Description of a few laboratory reproductions of some of the hydrogenation processes described in the literature now follows in Part II. These experiments were found to be necessary in order to become thoroughly acquainted with the details of the hydrogenation process and so form the basis for the original investigation of Part III. The rather meager description of the hydrogenation processes in the

[1] Ber. deutsch. pharm. Ges., **26**, 36–48 (1916).
[2] U. S. patent 1,171,902, February 15 (1916).

patents was found to be quite inadequate to enable one to go ahead with original work on the subject. Since such experimental details are not given in the literature, these preliminary experiments are not omitted here, but are described in sufficient detail to enable others to profit by what was actually done in this laboratory.

II. EXPERIMENTAL REVIEW OF A FEW KNOWN PROCESSES

Nickel Catalyst

Twenty grams of nickel nitrate were dissolved in 120 cc of distilled water and 20 grams of finely ground pumice were thoroughly stirred into the solution. The mixture was placed on a steam-heated sand bath to evaporate off the water. The cake formed was thoroughly ground in a mortar. The pulverized mixture was heated in a casserole to dull redness, with constant stirring, until the brown fumes of nitrogen dioxide were no longer evolved. The black mixture of pulverized nickel oxide and pumice was transferred to a hard-glass tube which was placed in an air bath at 350° C. A current of hydrogen was passed through the tube which was constantly rotated so as to secure intimate contact of the hydrogen and nickel oxide. After three hours' treatment in this manner, the material was allowed to cool to room temperature in the hydrogen atmosphere.

The cooled catalyst was introduced into 200 cc of cottonseed oil which had been previously heated to 100° C and treated with a rapid current of hydrogen for a few minutes. In order to avoid contact with the air, the transfer of this catalyst was accomplished by opening one end of the tube, containing the catalyst, under the surface of the oil and passing hydrogen into the other end of the tube. The charge of oil and catalyst was transferred to the apparatus of Fig. 3, in which the hydrogenation was carried out.

The bath was heated to 180° C and hydrogen from a pressure tank was bubbled through the cottonseed oil. Samples were taken at intervals of an hour. At the end of the fourth hour it was found that the oil had become semi-solid

on cooling to room temperature. At the end of five hours it solidified at room temperature. At the end of six hours the sample had a melting point of 35° C.

Cobalt Catalyst

Twenty grams of cobalt nitrate were dissolved in 120 cc of hot distilled water and 20 grams of powdered pumice were mixed with this solution. The mixture was then treated in the same manner as the foregoing preparation of the nickel catalyst. Two hundred cc of cottonseed oil were hydrogenated at 180° C with this cobalt catalyst in the apparatus of Fig. 3 and samples were taken at hour intervals.

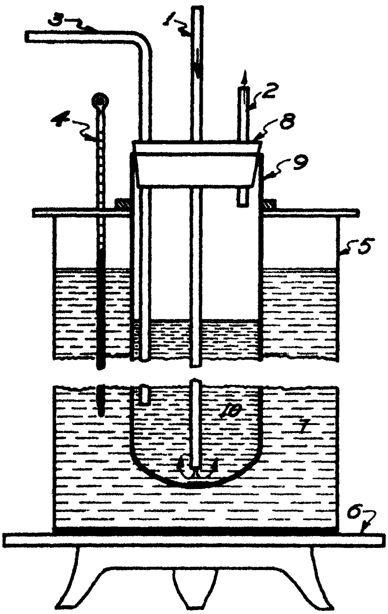

Fig. 3

It was found that a sample, at the end of six hours, became semi-solid at room temperature. At the end of seven hours the oil solidified at 25° C. After eight hours' hydrogenation the sample melted at 30° C. Further treatment did not raise the melting point. The nickel seemed to be the more efficient catalyst, both as to time and also as to the percentage yield of saturated oil.

Nickel-Cobalt Catalyst

Ten grams of nickel nitrate and 10 grams of cobalt nitrate were dissolved in 120 cc of hot distilled water. The water was evaporated off and the residue treated in the same manner as the cobalt and nickel residues just mentioned. The catalyst obtained in this case was used for reducing 200 cc of cottonseed oil in apparatus of Fig. 3. It was found that samples taken at hour intervals had a higher melting point

than the corresponding samples when cobalt or nickel was used alone. In this case the oil became semi-solid at room temperature after two hours' treatment with hydrogen. In three hours the oil solidified at 25° C. At the end of five hours it melted at 42° C. On further treatment the melting point remained unchanged, showing that equilibrium had been reached.

Iron Catalyst

Twenty grams of ferric chloride were dissolved in distilled water and 15 grams of powdered pumice were stirred into the solution. While rapidly stirring, the required amount of sodium carbonate solution was added to precipitate the iron. The solid was filtered off, washed with warm distilled water, dried, heated to drive off the carbon dioxide, placed into a hard glass tube and heated to 350° C in a current of hydrogen. After five hours of the latter treatment no more water was given off. Without admitting air to the catalyst, the iron pumice mixture was transferred to 200 cc of previously heated cottonseed oil The mixture was placed into the apparatus of Fig. 3 and hydrogen bubbled through it at 180° C for ten hours. A sample taken after ten hours showed a reduction of the iodine number from 108 to 90. The operation was continued for 20 hours. The iodine number was thus finally reduced to 85.

The experiment was repeated by precipitating the iron as ferric hydroxide with ammonium hydroxide. In this case the iodine number was reduced to 84.5 in 20 hours.

Iron-Nickel Catalyst

Five grams of nickel chloride and 15 grams of ferric chloride were dissolved in distilled water. The remaining procedure was identical with that of the iron catalyst just described. The iodine number of 200 cc of cottonseed oil treated with this agent and hydrogen at 180° C in the apparatus of Fig. 3 was reduced to 75 in 8 hours, but it could not be lowered by more prolonged treatment.

Other Iron Mixture Catalysts

Iron-cobalt and iron-copper were analogously tried with little success.

These results are in accord with those reported in Ellis' "Hydrogenation of Oils," p. 146. The activity of nickel, cobalt and iron as oil-hardening agents diminishes in the order named.

III. EXPERIMENTAL INVESTIGATIONS

Having thus successfully duplicated several of the processes recorded in the literature, it was decided to proceed to find new catalysts, and study the best conditions for employing them. Zinc salts were successfully used in the following manner:

1. Zinc Catalyst

Fifteen grams of zinc nitrate were dissolved in distilled water. To this solution eight and one-half grams of sodium carbonate were added to precipitate zinc carbonate. The zinc carbonate was filtered off and washed with distilled water to remove all traces of the sodium salts.

To obtain zinc oxide the carbonate was heated at 300° C in a porcelain dish over a Bunsen burner, so as to drive off the carbon dioxide. The zinc oxide was reduced with hydrogen at 350° C to 450° C for five hours. During the reducing process the hot zinc substance changed from yellow to a gray color. A cooled sample of this material when treated with hydrochloric acid liberated hydrogen, thus showing that metallic zinc was present.

The zinc catalyst was transferred into 200 cc of previously heated cottonseed oil, by opening one end of the tube containing the catalyst under the surface of the oil. The hydrogenation was carried out at 180°–190° C in the apparatus shown in Fig. 3. It was found difficult to keep a good suspension of zinc in the oil. After eight hours of hydrogenation, a product was obtained which appeared as a brownish semisolid at room temperature.

2. Zinc, Aluminum Catalyst

In order to secure a better suspension of the catalyst, the zinc carbonate was next precipitated in the presence of powdered aluminium in suspension. In this case three grams of the aluminium were stirred into the zinc nitrate solution before adding the sodium carbonate. The remainder of the procedure in preparing this catalyst was identical with the preparation of the preceding catalyst. Two hundred cc of cottonseed oil were hydrogenated with this catalyst in the apparatus shown in Fig. 3. In this case a good suspension was obtained on rapidly bubbling hydrogen through the mixture. Samples were withdrawn at one hour intervals with the following results, shown in Table I.

No of Sample	Time of Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refrac Index 40° C (Abbe
Orig. oil	– –	liquid	108.0	195 0	1 4642
1	4 hr.	liquid	96.2	—	1 4641
2	5 hr.	liquid	85 4	– ·	1 4637
3	6 hr.	semi-solid	81.7	– ·	1 4650
4	7 hr.	24.0	79.1	—	1 4616
5	8 hr.	28.0	78 6	—	1.4605
6	10 hr.	29.8	63 0	194 5	1 4600
7	12 hr.	29 9	63 0	194 0	1.4600

After the hydrogenation, the oil in the apparatus was kept at 70° C over night to allow the catalyst to settle. The clear oil was siphoned off and 200 cc of previously heated oil was poured into the apparatus. This second charge was then hydrogenated at the same temperature as the first quantity. Samples were siphoned off at one hour intervals. The results are given in Table II.

By comparing corresponding samples in Tables I and II it is seen that they agree fairly well. Some discrepancies do occur. For instance, sample 6 in Table I has a melting point of 29.8° C with an iodine number of 63. The corresponding

TABLE II

No. of Sample	Time of Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refrac Index 40° C
Orig. oil	—	liquid	108.0	195.6	1.4642
1	4 hr.	liquid	95.5	—	1.4638
2	5 hr.	liquid	85.5	—	1.4635
3	6 hr.	semi-solid	82.0	—	1.4625
4	7 hr.	25.0	80.0	—	1.4620
5	8 hr.	29.3	63.5	—	1.4600
6	10 hr.	29.4	63.0	193.2	1.4601

sample in Table II has a melting point of 29.0° C and an iodine number of 62. Unavoidable experimental error is undoubtedly the cause of these differences.

It was found that ten hours of hydrogenation under the conditions used brought about the maximum reduction of the unsaturated oil. No further addition took place on continued treatment.

The iodine number in all cases of this research was determined by the Hanus method. The melting point of the hardened oil was determined by allowing the capillary tubes containing the solidified fats to remain in a freezing mixture twelve hours before introducing them into a water bath to note the temperature at which the fat became transparent. The index of refraction was determined by an Abbé refractometer at 40° C. The saponification number was obtained in the usual way by saponifying in alcoholic potash.

3. Aluminum as Catalyst

Since the aluminum was used in connection with the zinc in preparing the catalyst in the preceding case, the question arose whether aluminum might not be responsible for the increased activity of the catalyst. Three grams of powdered aluminum were heated from 350° C to 450° C in a current of hydrogen for five hours. It was transferred without coming in contact with the air to 200 cc of previously heated cottonseed oil. The mixture was placed into the apparatus of Fig. 3,

heated to 180°–190° C and hydrogen bubbled through the oil for 10 hours. Upon cooling a sample in ice water, no sign of hardening appeared.

4. Zinc, Powdered Charcoal Catalyst

A catalyst was prepared in the same manner as in (2), only that 5 grams of activated powdered charcoal were substituted for the aluminum. Two hundred cc. of previously heated oil were mixed with the catalyst, and treated with hydrogen in the apparatus of Fig. 3. After 15 hours' treatment and cooling in ice water, only a slight thickening of the oil appeared. The results were not as good as when zinc was used alone in (1) above.

5. Zinc, Pumice Catalyst

In this case the preparation of the catalyst, and the hydrogenation process was a duplication of procedure 2, except that powdered pumice was substituted for the aluminum. After bubbling hydrogen through the oil for 15 hours a product was obtained which solidified at 40° C, but no further reduction took place.

From these experiments it appears that aluminum, when used in conjunction with zinc, has some specific action even though when used alone it produces no reduction of the unsaturated oil with hydrogen.

On the other hand, pumice which was found to act as a good carrier when used with nickel, retards the catalytic action of zinc.

6. Zinc Aluminum Catalyst prepared from Zinc Nitrate

Fifteen grams of zinc nitrate, fifty cc of distilled water and two grams of powdered aluminum were mixed in a solution. After evaporating to dryness, and then heating to dull redness to drive off oxides of nitrogen, the residue was reduced at 350° C to 450° C in a stream of hydrogen for five hours.

The catalyst was added to 200 cc of previously heated cottonseed oil. The mixture was placed into the apparatus of Fig. 3 and heated to 190° C. Hydrogen was bubbled

through the mixture for 10 hours. On cooling a sample, no congealing was apparent.

The relatively high temperature required to break down the nitrate to the oxide of zinc is perhaps the cause of producing an inactive zinc catalyst from the nitrate.

7. Bismuth, Charcoal Catalyst

Ten grams of bismuth subnitrate were dissolved in distilled water slightly acidified with nitric acid. To the solution three grams of powdered activated charcoal were added. While rapidly stirring, six grams of previously dissolved sodium carbonate were slowly added. The precipitate was transferred to a filter, washed to remove all the sodium salts, and dried at 150° C. To drive off the carbon dioxide, the mixture was heated to 325° C for two hours. Reduction of the oxide was carried out in a hard glass tube at 350° C in a current of hydrogen from a pressure tank. Without exposure to the air the catalyst was transferred to 400 cc of previously heated cottonseed oil.

The charge of oil and catalyst was placed into the apparatus of Fig. 4, in which hydrogenation may be carried on under pressures up to five atmospheres.[1] Experiments were carried out with different combinations of temperatures and pressures to ascertain the best conditions for hardening cottonseed oil, with the catalyst in question. The results of these experiments are as follows:

A. Hydrogenation at 160° C and 30 lb. pressure. Samples of oil were withdrawn from the apparatus at one hour intervals up to twelve hours. In all the cases the oil showed no signs of solidifying on being cooled to 5° C.

B. Hydrogenation at 160° C and 40 lb. pressure. Samples taken at hour intervals gave negative results, i. e., none of them solidified on being cooled as in A.

C. Hydrogenation at 160° C and 50 lb. pressure. In this case samples were taken in the same manner as in A and B. The results again were negative.

[1] This apparatus was obtained from Sieck & Drucker, Chicago.

D. Hydrogenation at 160° C and 60 lb. pressure. The pressure was then raised to the maximum capacity of the apparatus, i. e., 60 lb. The samples taken as in A did not show any signs of solidifying.

E. Hydrogenation at 170° C and 30 lb. pressure. The temperature was then raised to 170° C and the pressure

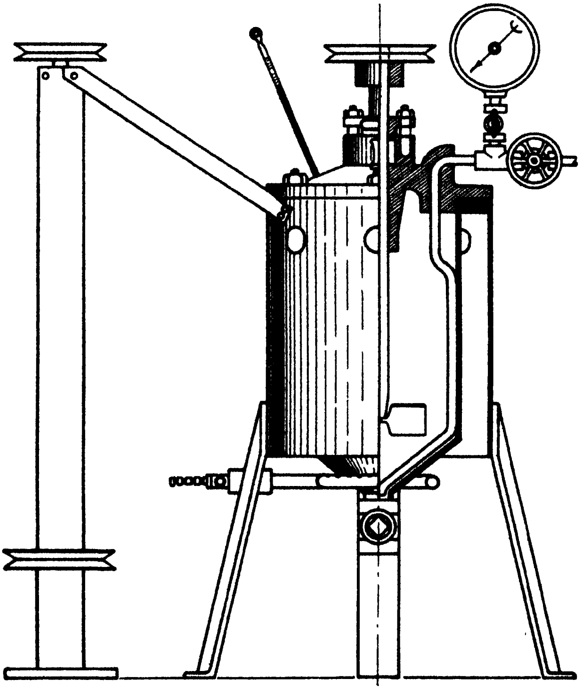

Fig. 4

varied from 30 lb. to 60 lb. Samples obtained while working at 30 lb. pressure and 170° C showed slight signs of hardening on being cooled. This was especially true in the tests made on samples taken after the sixth hour interval.

F. Hydrogenation at 170° C and 40 lb. pressure. Samples taken at hour intervals were cooled as in the previous cases. The results were the same as in E.

G. Hydrogenation at 170° C and 50 lb. pressure. Tests

made on samples in this case showed signs of slight hardening as in E and F.

H. Hydrogenation at 170° C and 60 lb. pressure. The pressure was next raised to its maximum. Tests made on samples gave the same results as under G.

I. Hydrogenation at 180° C and 60 lb. pressure. The pressure in this case was kept at 60 lb. and the temperature was slowly raised from 170° C to 180° C. When 180° C was reached, it was observed that the temperature of the oil mixture suddenly rose to 185° C, even when all external heating was removed. The temperature then gradually rose to a maximum of 190° C. It remained there for one-half hour and then slowly lowered to 175° C in one hour. External heat was again applied to raise the temperature to 180° C. A sample taken at the end of six hours and cooled was found to solidify into a dark brown mass. On remelting and filtering the sample to remove the catalyst, it was found that the oil had a melting point of 25° C. Samples taken at the end of eight hours had a melting point of 28° C. Further treatment of the oil failed to raise the melting point. In all these samples it was observed that the oil had a burned odor, whereas when heated to 170° C, as in H, no such odor was noticeable.

An attempt was made to determine the cause of this charring, by keeping the temperature constant and altering the pressure. A new charge of oil and catalyst was placed into the apparatus of Fig. 4. Hydrogen was allowed to bubble through the mixture while the temperature was slowly raised to 180° C. When 180° C was reached, the temperature again suddenly rose to 185° C, and then slowly continued to rise until a maximum of 190° C was reached. After one-half hour it gradually receded as in case I. External heat was again applied, and the hydrogenation was continued for ten hours. A sample taken at the end of seven hours had a melting point of 26° C. A sample at the end of eight hours had a melting point of 28° C, which was the maximum melting point obtainable even on continued hydrogenation. The

oil in this case also had a dark brown color and a charred odor.

From the last two experiments, i. e., hydrogenating at 180° C and 60 lb. pressure, and 180° C and atmospheric pressure, it is clear that pressures of five atmospheres did not aid the hydrogenation of cottonseed oil, when bismuth was used as the catalyst. It was also noted that the pressure had nothing to do with the charring of the oil, for the charred odor was the same when the operation was carried out under atmospheric pressure. Since the apparatus in Fig. 4 is heated with a gas flame it was believed that superheating might cause the charring of the oil. This was actually shown to be the case, when a charge of oil and catalyst was placed into the apparatus of Fig. 3 in which a glycerine bath was always used for heating the oil. In this case the charge was hydrogenated at 180° C by bubbling hydrogen through the mixture. Samples were removed at one hour intervals. The oil solidified into a white fat, when cooled to room temperature. No charred odor could be detected in this case. This bears out the statement made above, that superheating of the apparatus of Fig. 4 caused decomposition of the oil. The important constants of the hardened oil are given in Table III below.

It was next decided to ascertain the duration of the catalyst's activity. To do this, the clear, oily liquid was siphoned off from the catalyst, and a new charge of two hundred cc of cottonseed oil was added. The temperature was controlled at 180° C and a current of hydrogen was rapidly bubbled through the mixture. The results are recorded in Table IV.

The same catalyst was again used with a third charge of cottonseed oil. These results are shown in Table V.

The bismuth-charcoal catalyst used in the three experiments (cf. Tables III, IV and V) shows concordant results when corresponding samples of Tables III, IV and V are compared. The slight variations fall within the range of experimental error. In Table V it is seen that the catalyst has declined in activity. The minimum iodine number in this table is 70, whereas in Table IV the lowest iodine number is 63.8.

TABLE III

No. of Sample	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refractive Index 40° C (Abbé)
Orig. Oil	—	—	108.0	195.0	1.4642
1	4	—	98.0	—	1.4641
2	5	—	90.0	—	1.4640
3	6	semi-solid	85 2	—	1.4636
4	7	25°	77.0	—	1.4618
5	8	28°	64.5	—	1.4613
6	10	28°	65.2	193.8	1.4612

TABLE IV

No. of Sample	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refractive Index 40° C (Abbé)
1	4	—	96.0	—	1.4640
2	5	—	89.0	—	1.4638
3	6	semi-solid	86.0	—	1.4636
4	7	27.0	75.0	—	1.4616
5	8	28.2	64.0	—	1.4612
6	9	28.2	63.8	1.950	1.4611

TABLE V

No. of Samples	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refractive Index 40° C (Abbé)
1	4	—	97.0	—	1.4641
2	5	—	91.0	—	1.4640
3	6	semi-solid	84.5	—	1.4635
4	7	25.0	76.2	—	1.4618
5	8	26.0	70.0	—	1.4615
6	10	26.0	70.1	194.1	1.4613

Since small amounts of metallic bismuth have no toxic effects upon the human body, it was hoped that a good active catalyst might be prepared from this element. This would eliminate the necessity of removing small traces of the catalyst, as in the case when nickel is used for hardening oils intended as lard substitutes. The results which were obtained with

bismuth in this research indicated that equilibrium is reached too soon between the olein and the stearine formed, i. e., the percentage of saturation cannot be carried far enough to completion for preparing lard substitutes.

Perhaps a good bismuth catalyst might be prepared by other methods, such as replacing the metal from a solution by some metal farther up the scale of the electrolytic series. This would eliminate high temperatures in preparing the catalyst and so might produce an active, and at the same time non-poisonous, catalytic body. On account of lack of time this method of preparing a bismuth catalyst was not undertaken.

In preparing a nickel catalyst from the nitrate, a glowing temperature is required to remove the oxides of nitrogen. Then to reduce the nickel oxide with hydrogen a temperature of 350° C must be used. Nickel catalysts heated above 350° C in their preparation are generally inactive in hydrogenating processes at temperatures below 180° C and atmospheric pressure. With this fact in mind, it was undertaken to prepare a nickel catalyst at lower temperatures than those reported in the literature. It was believed that a catalyst prepared at a low temperature would hydrogenate cottonseed oil below 180° C, and thus eliminate all danger of decomposing the oil during the process of hardening. This attempt was successful, as will be seen in 8 and 10 below.

8. Replaced Nickel as Catalyst

Chemically pure granulated zinc was placed into a saturated solution of nickel chloride. At the end of three hours a dark coating of nickel was deposited upon the surface of the metallic zinc. This zinc-nickel material was washed with previously boiled warm water to remove any adhering nickel chloride. The substance was dried in an atmosphere of hydrogen at 125° C for one hour. The surface had a black velvety appearance. This catalyst was transferred to some previously heated cottonseed oil and the mixture was treated by bubbling hydrogen through it at 150° C in the apparatus of Fig. 3. A sample taken at the end of one hour showed the

effects of hardening. The hardened product had a slight brownish tinge, but was much lighter than that obtained with the zinc catalyst. The results of this run are recorded in Table VI. It was found that the same catalyst can be used for hardening several successive charges of oil without showing any decrease in its activity. Four such runs were made. The data are given in Tables VI, VII, VIII and XI, respectively.

TABLE VI

No. of Samples	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon Number	Refractive Index 40° C (Abbé)
Orig. oil		liquid	108.0	195	1.4642
1	2	liquid	96.3		1.4638
2	3	semi-liquid	90.2	—	1.4638
3	4	26.3	82.0	—	1.4629
4	5	36.5	61.5	—	1.4615
5	6	37	62	193.8	1.4600

TABLE VII

No. of Samples	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon Number	Refractive Index 40° C (Abbé)
Orig. oil	—	liquid	108.0	195	1.4642
1	2	semi-liquid	90	—	1.4637
2	3	27	86	-	1.4635
3	4	27.9	66.3		1.4617
4	5	37.2	62	—	1.4601
5	6	37.1	61	193.2	1.4601

TABLE VIII

No. of Samples	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refractive Index 40° C (Abbé)
Orig. oil	—	liquid	108.0	195	1.4642
1	2	semi-liquid	94.0	—	1.4637
2	3	23.3	81.2	—	1.4632
3	4	28.4	68.3	—	1.4620
4	5	37.0	57.0	—	1.4595
5	6	37.2	57.2	195	1.4598

TABLE IX

No. of Samples	Hours Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon Number	Refractive Index 40° C (Abbé)
Orig. oil	--	liquid	108.0	195	1 4642
1	2	semi-liquid	92.3	--	1.4638
2	3	25.2	79.1	—	1 4620
3	4	29 3	65.0	—	1 4615
4	5	35.0	60.0	-	1 4600
5	6	36.4	59.4	-	1.4598
6	8	36 5	60.1	194 2	1.4596

A study was made of the optimum temperature for hydrogenating cottonseed oil with the replaced nickel-zinc catalyst. Fifty cc samples of previously heated cottonseed oil were treated by bubbling hydrogen through the oil in the presence of the above catalyst. Runs were made at 150° C, 160° C, 170° C, 180° C and 190° C. Table X contains the results.

TABLE X

Temperature °C	Time in Hours	Iodine Number (Hanus)	Melting Point °C	Remarks
150	4	85 1	27 5	White solid
160	4	70 2	29 0	White solid
170	4	68 3	33.2	White solid
180	4	66.2	35.2	White solid
190	4	66.1	35 0	Brownish colored Slightly charred

A study of Table X reveals the fact that 180° C is the optimum temperature for hardening the cottonseed oil when the process is carried on at atmospheric pressure. At this temperature the action is completed in less time than at lower temperatures, and at the same time no decomposition of the oil occurs. This fact is indicated by the melting point and iodine number.

9. Granulated Zinc as Catalyst

Five grams of arsenic-free granulated zinc were treated with a current of hydrogen at 125° C for one hour. One

hundred cc of previously heated cottonseed oil were added to the catalyst. The mixture was hydrogenated in the apparatus of Fig. 3 at 180° C for ten hours. On cooling the oil to room temperature no apparent hardening was noted. This demonstrates the fact that granulated zinc cannot be used alone in hydrogenating cottonseed oil.

It is clear then as a result of this study that metallic nickel deposited upon arsenic-free granulated zinc is a new catalyst which is more efficient at temperatures below 180° C and atmospheric pressure, than any other nickel catalyst thus far reported in the literature.

10. Nickel Catalyst from Nickel Chloride

Ten grams of Kahlbaum's C. P. nickel chloride were pulverized, placed into a hard glass tube, and subjected to a current of hydrogen at a temperature from 180° C to 250° C. When 180° C was reached it was noted that silver chloride was precipitated by passing the escaping gas through silver nitrate solution. The temperature was gradually raised to 250° C and kept there until no more silver chloride was deposited. The residue in the reducing tube has a slightly brownish black color.

This residue was transferred without contact to the air to 200 cc of heated cottonseed oil and the mixture was introduced into the apparatus of Fig. 3.

While hydrogen from a pressure tank was being slowly bubbled through the mixture the bath was brought to 180° C and then the current of hydrogen was increased to a rapid bubbling. Samples were taken at hour intervals. It was found that this catalyst reduced the oil to a solid mass in six hours. The results of the study are found in Table XI. Since this catalyst had been prepared at a much lower temperature than the catalyst obtained by reducing nickel oxide (350° C), it was decided to attempt to hydrogenate the oil at 150° C, as in the case of nickel replaced by zinc in 9 above.

In Table XI it is seen that a solid fat was obtained in five hours. Runs were then made in the apparatus of Fig. 3

with the reduced nickel chloride catalyst at temperatures ranging from 150° C. to 190° C. These results are found in Table XII.

TABLE XI

Sample	Hours of Treatment	Melting Point °C	Iodine Number (Hanus)	Sapon. Number	Refractive Index 40° C (Abbé)
Orig. oil	—	liquid	108.0	195	1.4642
1	3	liquid	94.0	—	—
2	4	semi-solid	80.4	—	—
3	5	27	78.1	—	—
4	6	30	70.3	—	1.4619
5	7	34	61.3	—	1.4600
6	8	34	60.0	193	1.4601

TABLE XII

Temperature	Time in Hours	Iodine Number (Hanus)	Melting Point °C
150	5	106.0	liquid
160	5	85.0	semi-solid
170	5	79.2	22
180	5	66.5	30
190	5	66.8	30.2

The data of Table XI show that the catalyst prepared by reducing nickel chloride is quite active. In five hours cottonseed oil is hardened to a melting point of 27° C. In seven hours the melting point of the hardened oil is raised to 34° C. The latter product has a good consistency for market purposes.

From Table XII it is seen that the catalyst hardens the oil at 170° C. In five hours the iodine number is reduced from 108 to 79.2. The most efficient temperature, however, is 180° C, for in this case time is saved, and at the same time the oil is not decomposed by excessive heating.

IV. SUMMARY AND CONCLUSIONS

The object of this research, as stated in the beginning, was to find new catalytic agents for hydrogenating cotton-

seed oil. On reviewing the results obtained the following conclusions may be drawn:

1. Nickel is the most efficient common metal catalyst for hardening cottonseed oil. The fact that nickel is the best single metal catalyst for hydrogenating oils is in harmony with what others have found.

2. A half-and-half nickel-cobalt catalyst was found to be more active than either metal, when used alone.

3. Two new nickel catalysts were prepared, namely:

(*a*) Nickel deposited upon arsenic-free granulated zinc in a saturated solution of nickel chloride. This catalyst was prepared at lower temperatures than other nickel catalysts. It hardens cottonseed oil, under atmospheric pressure, at lower temperatures than any other nickel catalysts hitherto described.

(*b*) Nickel chloride reduced with hydrogen at 180° C to 250° C. This is also a good catalyst. It brings about hydrogenation of cottonseed oil fairly well at 170° C.

4. Zinc carbonate freshly precipitated in the presence of suspended powdered aluminum, and reduced at 350° C to 504° C makes a fairly good catalyst for hardening cottonseed oil.

5. Bismuth precipitated upon charcoal and reduced with hydrogen at 350° C is a fairly active agent for reducing unsaturated oils.

Chemical Laboratory
University of Wisconsin
Madison, November, 1920

DENSITY OF HYDROCHLORIC ACID

BY J. FITCH KING

Recently I had occasion to consult the literature for the density of 2 *N* HCl at 15° C referred to water at 4° C. This paper is intended to show the lack of agreement on data on the density of hydrochloric acid, a lack which may be typical of published density data in general, and to give the results of my own work on the density of hydrochloric acid.

From each investigator's work I have selected the concentration nearest to 2 *N* and from the density of that acid have calculated the density of 2 *N* acid, assuming $\frac{\Delta D}{\Delta C} = K$ as given in the following table:

Investigator	Percent HCl	N	Density 15° C	$\frac{\Delta D}{\Delta C}$
Lunge	12.38	3.60	1.0609	0.00494
	9.99	2.87	1.0491	–
	7.84	2.23	1.0384	0.00498
	5.18	1.46	1.0251	0.00500
	2.93	0.81	1.0140	0.00493
Cheneveau	11.93	3.46	1.0587	
	8.12	2.31	1.0398	0.00496
	4.13	1.15	1.0200	0.00497
Kohlrausch (18°)	9.81	2.82	1.0487	-
	4.74	1.33	1.0236	0.00495

Average, 0.00496

$\frac{\Delta D}{\Delta C}$ varies in the above range of concentration from the average value by as much as 0.00004. 2 *N* Hydrochloric acid contains 7.05 percent of HCl as calculated from Lunge's figures. So in calculating the density of 2 *N* HCl even from the density of 2 percent acid or of 12 percent acid, an error of no greater than 5 × 0.00004 or 0.0002 could be introduced. Most of the conversions covered a much shorter range.

In converting from a given temperature to 15° C, I have used the temperature coefficient given by Lunge and Marchlewski[1] of 0.00023 per degree, which is in accord with the value given by Schuncke.[2] When unable to discover whether water at the temperature of the experiment, at 4° C, or at 0° C, was used as the standard of reference, I have used the temperature which brings the result nearest the average of the results. In no case did the temperature difference exceed 5°; hence a ten percent error in the temperature coefficient could not change the calculated density by more than one unit in the fourth decimal place.

Thus for example:

Given that:

7.15 percent HCl has a density of 1.0357 at 15.5° C referred to water at 15.5° C.

Density of H_2O at 15.5° C is 0.99905.

$1.0357 \times 0.99905 = 1.0347 = d$ referred to H_2O at 4° C.

$1.0347 + (0.5 \times 0.00023) = 1.0348 = D^{15°}_{4°}$.

$1.0348 - [(7.15 - 7.05) \times 0.00496] = 1.0343$.

Result: Density of 2 *N* HCl at 15° C referred to water at 4° C is 1.0343.

Also having found that $1.0348 = D^{15°}_{4°}$ of 7.15 percent HCl calculations could be made as follows:

Since one litre at 15° C contains 1034.8 grams
$0.0715 \times 1034.8 = 73.98 =$ wt. of HCl per litre.

Now one liter of 2 *N* HCl contains 72.94 gram HCl.

$$0.0348 \times \frac{72.94}{73.98} = 0.0343.$$

$$\text{Density} = 1.0343.$$

All the data from the literature were given to four or five places of decimals. The literature references are given at the end of the article.

[1] Zeit. angew. Chem., 1891, 133.
[2] Zeit. phys. Chem., 14, 331 (1894).

Determined by	Conc. of HCl	Density	Temp. °C	Referred to water at °C	Calculated Density of 2 N HCl $\frac{15\ °C}{4\ °C}$
Freund[17]	2 N	1.0356	15.65	4.0	1.0357
Kolb[3]	6.26%	1.0310	15.0	0.0	1.0349
Edwards[7]	5.31%	1.0261	16.0	4.0	1.0347
Schuncke[8]	6.49%	1.0340	15.0	4.0	1.0346
Ure[1]	6.52%	1.0318	15.0	4.0	1.0345
Lunge and Marchlewski[5]	7.84%	1.0384	15.0	4.0	1.0344
Chèneveau[16]	8.12%	1.0398	15.0	4.0	1.0344
Mfg. Chem. Ass'n.[20]	7.15%	1.0357	15.5	15.5	1.0343
Worden and Motion[14]	5.71%	1.0274	15.0	4.0	1.0340
Graham[2]	7.90%	1.0380	15.5	—	1.0340
Forchheimer[13]	7.17%	1.0334	20.0	4.0	1.0340
Ferguson[15]	10.74%	1.0525	15.0	4.0	1.0339
Pickering[6]	6.38%	1.0315	15.0	15.0	1.0339
Kohlrausch[9]	9.81%	1.0486	18.0	18.0	1.0339
Barnes and Scott[11]	6.56%	1.0305	19.5	4.0	1.0338
Loomis[10]	1 N	1.0165	18.0	4.0	1.0337
Sidersky[19]	5.00%	1.0242	15.0	15.0	1.0336
Conroy[12]	1 N	1.0163	18.0	4.0	1.0333
Jones[18]	2 N	1.0341	20.0	4.0	1.0331
Kohlrausch[4]	1.0014 N	1.0161	18.0	4.0	1.0328

Experimental

In my own determination of the density of hydrochloric acid, the Davis pycnometer[1] was used. Conductivity water was prepared by treating distilled water with potassium dichromate, acidified with sulphuric acid. This was distilled into baryta water and again distilled. A block tin condenser was used and a trap was inserted between the last still and the condenser. Grasselli "strictly chemically pure" hydrochloric acid was distilled into this conductivity water. The resulting acid solution was stored in an old hydrochloric acid bottle which had been cleaned and steamed out. The pycnometers were thoroughly cleaned and steamed out and then dried by passing dry air through them. The freshly prepared conductivity water was used to determine the volumes of the pycnometers. The thermostat used was regulated at 15° C to ± 0.05° (thermometer standardized by the Bureau of Standards). Two pycnometers were used and the determinations with each pycnometer were run in triplicate. The filled pycnometers were allowed to remain in the thermostat for twenty minutes. After adjustment, the ends were capped and the pycnometers were hung in the balance case until the weight was constant to four-tenths of a milligram. Two different concentrations of acid were used so as to determine the concentration coefficient, and the density of one of the concentrations was measured at two temperatures so as to determine the temperature coefficient.

The composition of the acid was found by the silver chloride method, using the Gooch crucible, two determinations being made of each concentration. The silver chloride precipitate was treated with hydrochloric acid and nitric acid and heated at 200° C until the weight was constant to ±0.0001 gram. The hydrochloric acid solution was weighed in weighing bottles with gas-tight ground glass stoppers to prevent any evaporation during weighing, care being taken that none of the solution came in contact with the capillary of the ground

[1] Jour. Am. Chem. Soc., 37, 1198.

glass stopper. Conductivity water was used in all the analytical work. The results of the investigation are given in the following tables.

Composition:

Analysis No.	Corrected weight of HCl solution in vacuum Grams	Corrected weight of AgCl in vacuum Grams	Weight of HCl Grams	Composition Percent
I A	2.0908	0.8158	0.2076	9 927
II A	2.1795	0.8502	0.2163	9 925
I B	2 9998	0.8418	0.2142	7.140
II B	3.0459	0.8543	0 2175	7.138

Density $\frac{15^\circ}{4^\circ}$

Pycnometer No	Corrected weight of water content in vacuum Grams	Volume Cc	Corrected weight of HCl solution content in vacuum Grams	Density
1 A	18.9762	18 9933	19 9182	1 04870
2 A	18.6070	18.6238	19.5308	1 04870
1 B	18 9762	18.9933	19.6543	1 03480
2 B	18 6070	18 6238	19.2717	1.03479
Density $\frac{20^\circ}{4^\circ}$				
1 C	18 9610	18.9952	19 6323	1.03354
2 C	18.5924	18 6259	19.2508	1.03355

Calculations as in above table on page 116. Results given to four places of decimals for comparison:

Conc. of HCl Percent	Density	Temp °C	Referred to water at °C	Calculated Density of 2*N* HCl at $\frac{15^\circ}{4^\circ}$
9.926	1.04870	15°	4°	1.0344
7.139	1.03480	15°	4°	1.0344
7.139	1.03355	20°	4°	1.0344

Calculation of concentration coefficient:

Percent HCl	N	Density $\frac{15°}{4°}$	$\frac{\Delta D}{\Delta C}$
9.926 7.139	2.854 2.023	1.04870 1.03480	0.004986

Calculation of temperature coefficient:

Percent HCl	Temp.	Density	$\frac{\Delta D}{\Delta T}$
7.139 7.139	15° 20°	1.03480 1.03355	0.000250

Discussion of Accuracy of Work

In determining the composition of the hydrochloric acid solutions, the silver chloride was weighed to two units in the fourth decimal place. This might involve an error of five units in the fifth decimal place in the weight of the HCl or about a 0.03 percent error which would effect the percent composition by two units in the third decimal place. A change in the composition of 1 percent changes the density 0.00496. An error of 0.002 in the percent composition would be equivalent to a change in the density of 0.00001.

The pycnometers were weighed to four units in the fourth decimal place. This could introduce an error of 0.002 percent, which would effect the density by 0.00002. The capillaries in the pycnometers were 0.12 cm in diameter and the meniscus was set to within 0.02 cm of the mark. This might introduce an error of 0.0002, which is within the error of weighing.

[1] Ure: Handwörterbuch prakt. Chemie., 99 (1825).
[2] Graham: Phil. Trans. (1850).
[3] Kolb: Comptes rendus, **74**, 737 (1872).
[4] Kohlrausch: Wied. Ann., **26**, 174 (1885).
[5] Lunge and Marchlewski: Zeit. angew. Chem., **1891**, 133.
[6] Pickering: Ber. deutsch. chem. Ges., **26**, 278 (1893).
[7] Edwards: Am. Chem. Jour., **16**, 629 (1894).
[8] Schuncke: Zeit. phys. Chem., **14**, 345 (1894).
[9] Kohlrausch: Wied. Ann., **53**, 33 (1894).

[10] Loomis: Wied. Ann., **60,** 550 (1897).
[11] Barnes and Scott: Jour. Phys. Chem., **2,** 546 (1898).
[12] Conroy: Proc. Roy. Soc., **64,** 315 (1898).
[13] Forchheimer: Zeit. phys. Chem., **34,** 28 (1900).
[14] Worden and Motion: Jour. Soc. Chem. Ind., **24,** 178 (1905).
[15] Ferguson: Jour. Soc. Chem. Ind., **24,** 781 (1905).
[16] Chèneveau: Ann. Chim. Phys., (8) **12,** 214 (1907).
[17] Freund: Zeit. phys. Chem., **66,** 555 (1909).
[18] Jones and Pearce: Carnegie Inst. Pub., 80 (1913).
[19] Sidersky: "Constantes Physico-Chimiques," p. 50.
[20] Mfg. Chemists' Ass'n. of U. S. A., "Scott's Standard Methods of Analysis."

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THE OSMOTIC CONCENTRATION AND ELECTRICAL CONDUCTIVITY OF THE TISSUE FLUIDS OF LIGNEOUS AND HERBACEOUS PLANTS[1]

BY J. ARTHUR HARRIS, ROSS AIKEN GORTNER AND JOHN V. LAWRENCE

I. The Osmotic Concentration of the Leaf Tissue Fluids of Herbaceous and Ligneous Plants

An examination of earlier literature on the osmotic concentration of plant tissue fluids shows various suggestions of a difference in the osmotic concentration of the leaf fluids of herbaceous and ligneous plants. As early as 1911 Fitting[2] noted from his plasmolytic studies on desert plants that the lowest osmotic pressures are found in annuals and the highest in shrubs.

The existence of a differentiation of ligneous and herbaceous plants with respect to the magnitude of the osmotic concentration of their tissue fluids was first demonstrated in a strictly quantitative manner by work on the sap of the plants of the spring flora of the Arizona deserts[3] in the neighborhood of the Desert Botanical Laboratory. Because of the strongly contrasted environmental conditions in these southwestern deserts the growth forms are sharply differentiated. Following as closely as possible Thornber's classification of the growth forms,[4] thereby obviating any possible question of personal equation in the classification of the plants, we find the results for freezing point lowering given in Table I.[5]

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[1] Studies carried out by the co-operation of the Department of Experimental Evolution and the Department of Botanical Research of the Carnegie Institution of Washington.

[2] H. Fitting: Zeit. Bot., 3, 209–275 (1911).

[3] J. Arthur Harris, J. V. Lawrence and R. A. Gortner: Phys. Res., 2, 1–49 (1916).

[4] J. J. Thornber: Pub. Carnegie Inst. Wash., No. 113, pp. 103–112 (1909).

[5] Harris, Lawrence and Gortner: Loc. cit., pp. 45–46. The averages in the table are averages of species determinations, not of species means.

TABLE I

Average Freezing Point Lowering, Δ, of Different Growth Forms from Various Habitats in the Arizona Deserts

Growth form	Arroyo	Canyons	Rocky slopes	Bajada slopes	Salt spots	All habitats
Trees and shrubs	1.476	1.867	1.857	2.895	4.008	2.340
Dwarf and half shrubs	1.380	1.615	1.701	1.942	2.850	1.733
Perennial herbs	1.128	1.150	1.415	1.636	—	1.357
Winter annuals	1.075	1.094	1.269	1.759	1.960	1.227

TABLE II

Actual and Percentage Difference in Freezing Point Lowering, Δ, of Tissue Fluids of Ligneous and Herbaceous Plants of the Arizona Deserts

Growth form	Arroyo	Canyons	Rocky slopes	Bajada slopes	Salt spots	All habitats
All species	1.156	1.047	1.516	2.197	3.095	1.594
Ligneous species	1.441	1.751	1.753	2.523	3.776	2.055
Herbaceous species	1.080	1.117	1.325	1.708	1.960	1.261
Difference	0.361	0.634	0.428	0.815	1.816	0.794
Percentage difference	25.05	36.20	24.41	32.30	48.09	38.63

It is clear that the concentration of the leaf tissue fluids of trees and shrubs is higher than that of dwarf shrubs and half shrubs. The freezing point lowering found in the tissue fluids of both perennial herbs and winter annuals is, without exception, less than that observed in either of the ligneous growth forms.

Combining the growth forms into two groups, ligneous and herbaceous (Table II), the freezing point lowering of the leaf tissue fluids of the herbaceous plants is seen to be less in every instance than that of the ligneous species from the same habitats. The percentage differences, calculated by using the value of the ligneous plants as a base, range from 24.4 to 48.1.

Unfortunately, it is impossible to group the plant species of a temperate mesophytic region or of a tropical region with ample moisture and uniform temperature in exactly the same way as those from a subtropical desert of the type in which our first investigation was carried out. Biennials, and species growing as either biennials or annuals, which are so conspicuous a feature of a mesophytic temperate flora are practically wanting in the desert. The dwarf shrubs and half shrubs which are so dominant as an element in the desert flora studied are not abundant in the flora of the Eastern United States. The herbaceous annuals, prominent in both the xerophytic and mesophytic nearctic region, are but sparingly represented in moist subtropical and tropical regions.

A uniform classification of growth forms is, therefore, impossible. Studies on the terrestrial vegetation of the Jamaican montane rain forest have shown the following results for the average of species averages of the freezing point depression[1] (Table III).

Without exception the values of Δ are higher for the ligneous than for the herbaceous species. The percentage differences, calculated as above, range from 22.1 to 30.3.

It is, therefore, fully demonstrated by these data from two geographically widely separated and climatically very

[1] J. Arthur Harris and J. V. Lawrence: Am. Jour. Bot., 4, 287 (1917).

TABLE III

Actual and Percentage Difference in Freezing Point Lowering, Δ, of the Tissue Fluids of Ligneous and Herbaceous Plants of the Jamaican Montane Rain Forest

Growth form	Leeward slopes	Leeward ravines	Ridge forest	Windward habitats	All habitats
All species	1.007	0.822	0.914	0.743	0.881
Ligneous species	1.089	0.901	0.958	0.805	0.952
Herbaceous species	0.812	0.628	0.718	0.627	0.700
Difference	0.277	0.273	0.240	0.178	0.252
Percentage difference	25.43	30.29	25.05	22.11	26.47

dissimilar regions (and by extensive unpublished series) that the leaf tissue fluids of ligneous plants are characterized by an osmotic concentration materially higher than that of herbaceous forms.

The magnitude of the specific electrical conductivity of the fluids must next be considered in comparison with osmotic concentration as measured by the freezing point lowering.

II. The Osmotic Concentration and Specific Electrical Conductivity of the Leaf Tissue Fluids of Herbaceous and Ligneous Plants of a Mesophytic Flora

The determinations here considered were made on the north shore of Long Island during 1914 and 1915. Leaf tissue was collected in large test tubes. After freezing in an ice-salt mixture[1] to render the tissue permeable, as has been shown to be necessary by Dixon and Atkins[2] and by ourselves.[3] The sap was extracted as completely as possible by pressure, cleared by centrifuging and the freezing point lowering, Δ, was determined in the usual manner. Correction was made for the ice separating on undercooling by the formula

$$\Delta = 0.0125\, u\, \Delta',$$

where u is the undercooling and Δ' the observed freezing point lowering in degrees.

The specific electrical conductivity, κ, of the sap was measured at 30° C in a Freas conductivity cell, standardized against $N/10$ KCl, which has a specific conductivity 0.01412 reciprocal ohms at 30°, by means of the ordinary meter bridge wire and resistance box of the physiological laboratory.

All determinations were made with as great care as possible, but there are many possible sources of error, and some selection of the constants to be used in the present paper seems

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[1] R. A. Gortner and J. Arthur Harris: Plant World, **17**, 49–53 (1914).

[2] H. H. Dixon and W. R. G. Atkins: Proc. Roy. Soc. Dublin, **13**, 422–433 (1913). Also in Notes Bot. Sch. Trin. Coll., Dublin, **2**, 154–172 (1913).

[3] R. A. Gortner, J. V. Lawrence and J. Arthur Harris: Biochem. Bull., **5**, 139–142, pl. 1 (1916).

desirable. To avoid weighting the species upon which more than a single determination had been made, species averages are used whenever possible. These were determined as follows. The whole of the data which had been accumulated at various times during the two years were arranged together by species and all determinations which seemed obviously open to criticism were thrown out. The determinations for each species were then averaged and the deviation of each determination from the average for the species was calculated. All numbers which showed a deviation of more than ± 20 percent for either Δ, κ, or κ / Δ, were discarded, and a new average with deviations $< \pm 20$ percent determined from the remainder.

The inclusion of determinations differing from the average by as much as ± 20 percent might at first seem to represent great laxness of selection. One must remember, however, that these variations represent more than the errors of experimental measurement. They include all the differences due to seasonal and environmental influence as well as the errors of random sampling in the collection of the tissues. Thus the limits chosen probably represent rather stringent instead of lax selection. The detailed data are shown in Table IV.

Determining the usual statistical constants from the protocols of measurements we have the accompanying results (Table V) for the three growth forms, and for a combination of the two groups of ligneous plants.

The constants in Table V show that the mean freezing point lowering of the leaf tissue is greater, although perhaps not significantly greater in comparison with its probable error, in arborescent than in shrubby species. The tissue fluids of both trees and shrubs are characterized by a far greater freezing point lowering than those of herbaceous plants. The differences between trees and herbs, shrubs and herbs, and all ligneous plants and herbs are everal times as large as the probable error of the difference and hence unquestionably significant.

TABLE IV

Protocols of Determinations[1]

Constants for Trees

	Δ	$\kappa \times 10^6$	$\kappa/\Delta \times 10^6$
Acer rubrum (2)	1.132	6585	7325
Aesculus Hippocastanum	0.722	10398	14401
Ailanthus glandulosa	1.480	15546	10504
Alnus rugosa (2)	1.368	9393	6863
Betula lenta	1.464	11080	7589
Betula lutea	1.221	10737	8833
Cynoxylon floridum (3)	1.119	12264	10957
Diospyros virginiana (2)	1.385	8586	6242
Gleditsia triacanthos (2)	1.250	11348	9083
Juglans cinerea	1.478	11802	8011
Padus virginiana (2)	1.754	8183	4659
Quercus coccinea	1.487	17287	11015
Quercus palustris	1.780	9871	5586
Quercus Prinus	1.655	12518	7568
Robinia Pseudacacia (3)	1.006	14364	14337
Salix alba vitellina	1.178	16513	14017
Tilia americana (2)	1.107	13814	12600
Vitis aestivalis	1.071	6107	5702
Vitis labrusca	0.892	6657	7463

Constants for Shrubs

Amorpha fruticosa	1.104	10063	9115
Ampelopsis Veitchii	0.863	11460	13279
Aronia atropurpurea	1.165	10140	8703
Azalea nudiflora (3)	0.998	10696	10701
Benzoin aestivale (4)	1.104	11755	10744
Berberis vulgaris	1.555	9001	5788
Berberis vulgaris purpurea	1.598	8563	5358
Clethra alnifolia (3)	0.786	11075	14119
Comptonia peregrina	1.211	8018	6620
Cornus alternifolia	1.205	11886	9863
Epigaea repens	1.085	9526	8779
Gaylussacia frondosa	1.310	8777	6700
Hibiscus Syriacus (2)	1.120	17317	15499
Lonicera tatarica	1.644	11979	7286
Myrica carolinensis (2)	1.135	8619	7578

[1] Species are grouped primarily according to growth forms, as discussed in the paper. For convenience of reference they are alphabetically arranged under each growth form. The number in parentheses shows the number of individual determinations averaged to obtain the species constant. Those without numbers represent one determination only.

TABLE IV (*Continued*)
Constants for Shrubs (*continued*)

	Δ	$\kappa \times 10^6$	$\kappa/\Delta \times 10^6$
Parthenocissus quinquefolia	0.943	8426	8935
Prunus sp. (2)	1.514	18084	12104
Rhus glabra (3)	1.286	12131	9475
Rosa virginiana	1.043	10190	9769
Rubus argutus (2)	1.199	11456	9483
Rubus hispidus	0.818	11841	14475
Sambucus canadensis (6)	1.065	15583	14670
Smilax rotundifolia	1.237	11466	9269
Solanum Dulcamara (4)	0.914	17327	19146
Sorbaria sorbifolia (2)	1.297	16119	12453
Toxicodendron Toxicodendron	1.135	10190	8977
Toxicodendron Vernix	1.391	9989	7181
Uva-ursi Uva-ursi	1.218	5856	4809
Vaccinium angustifolium	0.965	8449	8755
Vaccinium atlanticum	1.366	5896	4316
Vaccinium corymbosum	1.561	8038	5149
Vaccinium vacillans	0.948	6768	7139
Viburnum acerifolium (3)	1.057	13153	12429
Viburnum cassinoides	1.300	7467	5743
Viburnum dentatum (2)	1.272	11052	8899
Xolisma ligustrina (2)	0.977	9355	9730
Constants for Herbs			
Achillea lanulosa	0.815	16645	20423
Achillea Millefolium	0.738	13622	18457
Agrimonia gryposepala (3)	0.861	14508	16899
Agrimonia sp. (2)	0.875	13726	15726
Alsine media (4)	0.605	16388	27185
Ambrosia elatior	0.807	22250	27571
Ambrosia trifida	0.754	20072	26620
Anaphalis margaritacea (2)	0.940	19785	21140
Antenarria plantaginifolia	0.743	16987	22862
Anthemis Cotula	0.604	15671	25945
Aralia nudicaulis	1.386	9515	6865
Asclepias pulchra	0.593	13703	23116
Asparagus officinalis	1.545	18795	12165
Aster macrophyllus (2)	0.646	17075	27124
Aureolaria Pedicularia	1.411	19195	13603
Aureolaria villosa	1.174	16179	13781
Baptisia tinctoria (3)	1.016	7832	7752
Barbarea Barbarea (4)	0.785	17133	21983
Barbarea stricta (2)	0.795	16038	20181
Brassica juncea (2)	0.728	15836	21787

TABLE IV (*Continued*)
Constants for Herbs (*continued*)

	Δ	$\kappa \times 10^6$	$\kappa/\Delta \times 10^6$
Brassica napus	0.803	17897	22287
Brassica nigra	0.789	19257	24407
Cardamine pennsylvanica (2)	0.670	18141	27083
Carex scoparia	1.017	16447	16172
Chelidonium majus (4)	1.000	11345	11347
Chenopodium album	0.991	24054	24272
Chenopodium sp.	0.936	26845	28680
Chimaphila maculata	0.984	6349	6452
Chrysanthemum Leucanthemum (2)	0.967	15770	16305
Chrysopsis mariana (2)	0.806	14850	18447
Cichorium Intybus (3)	0.796	18711	23496
Cimicifuga racemosa	0.937	15235	16259
Circaea lutetiana (4)	0.489	10397	21363
Commelina communis	0.422	12176	28861
Convallaria majalis	0.829	12574	15167
Convulvulus arvensis	0.937	18272	19500
Crocanthemum canadense	0.741	8732	11784
Daucus Carota (2)	1.143	20394	17836
Deringa canadensis (2)	0.934	21182	22810
Dianthus Armeria	1.009	19038	18868
Erechtites hieracifolia	0.506	12422	24549
Erigeron annuus (3)	0.808	14070	17427
Erigeron ramosus	1.153	10355	8981
Eupatorium perfoliatum	0.583	13457	23082
Eupatorium trifoliatum	0.813	20372	25057
Euthamia graminifolia (2)	0.936	14846	15926
Euthamia tenuifolia	0.721	14936	20730
Fagopyrum Fagopyrum	0.540	13198	24440
Fragaria vesca americana	1.098	9384	8546
Fragaria virginiana	0.998	12828	12853
Galinsoga parviflora (2)	0.601	16392	27329
Galium Aparine (5)	0.722	12486	17365
Geranium maculatum (5)	0.768	9922	13000
Geranium pusillum	0.789	17400	22053
Geranium rotundifolium	0.888	17829	20077
Geum canadense (2)	1.192	19014	16128
Gratiola aurea	0.618	12518	20255
Hemerocallis fulva	0.940	9459	10062
Hieracium sp.	0.783	15990	20421
Hypericum mutilum	0.865	11599	13409
Hypericum perforatum (3)	1.002	12181	12239
Hypericum punctatum	0.833	12473	14973
Impatiens biflora (5)	0.518	11784	22857
Ionactis linariifolius	0.881	13566	15398

TABLE IV (*Continued*)
Constants for Herbs (*continued*)

	Δ	$\kappa \times 10^6$	$\kappa/\Delta \times 10^6$
Lactuca virosa	0.681	18264	26819
Lappula virginiana	0.644	15546	24139
Lathyrus latifolius (2)	0.942	10562	11219
Leontodon Taraxacum	0.707	13622	19267
Leonurus Cardiaca (4)	0.903	18654	20769
Leptilon canadense (2)	0.810	14509	17957
Lespedeza capitata	0.946	12323	13026
Lespedeza frutescens	1.035	7315	7067
Lespedeza hirta (2)	0.794	9734	12271
Lespedeza violacea	0.984	10834	11010
Lespedeza virginica	0.836	10566	12638
Linaria canadensis (3)	0.580	10495	18167
Linaria Linaria (2)	0.847	10232	12088
Lychnis alba	0.793	20680	26078
Lychnis dioica	0.711	18126	25493
Lycopodium obscurum	0.874	7928	9070
Lycopus sessilifolius	0 625	16120	25792
Lycopus virginicus (2)	0.538	13554	25234
Lysimachia Nummularia (2)	0.747	12907	17397
Lysimachia quadrifolia (3)	0.634	11070	17660
Lysimachia terrestris	0.717	9076	12658
Medeola virginiana (2)	0.833	13543	16371
Medicago lupulina	1.068	12371	11583
Melampyrum lineare (2)	1.164	15427	13248
Melilotus alba	1.119	10358	9256
Mentha citrata	0.751	13352	17807
Monarda didyma (2)	0.694	13636	19649
Monarda fistulosa	1.037	12574	12125
Nepeta Cataria	0.724	15740	21740
Nepeta hederacea (2)	0.650	12805	19743
Oenothera muricata	0.711	11284	15885
Oenothera Oakesiana	0.726	12181	16778
Ornithogalum umbellatum	0.713	9268	12998
Osmunda regalis	1.180	15925	13495
Panicum clandestinum	0.764	14877	19535
Persicaria Hydropiper	0.707	12225	17291
Persicaria Persicaria	0.607	11321	18650
Persicaria punctata	0.586	12473	21285
Phlox paniculata	0.737	14755	20020
Physalis heterophylla	0.704	15175	21555
Phytolacca decandra	0.726	14063	19370
Plantago lanceolata	0.867	13622	15711
Plantago media	0.775	18500	23870

TABLE IV (*Continued*)
Constants for Herbs (*continued*)

	Δ	$\kappa \times 10^6$	$\kappa/\Delta \times 10^6$
Plantago Rugelii	0.789	18192	23057
Polygonatum commutatum	1.014	10920	10769
Polygonum aviculara	0.593	11373	19178
Portulaca oleracea (2)	0.598	15962	26713
Potentilla canadensis	0.935	12225	13074
Potentilla monspeliensis	1.050	18205	17338
Prunella vulgaris	0.638	9740	15266
Pteridium aquilinum	1.555	15671	10077
Ranunculus abortivus	1.231	10876	8835
Ranunculus bulbosus (2)	1.016	12397	12203
Ranunculus recurvatus (2)	0.998	10574	10690
Ranunculus sceleratus	0.941	17264	18346
Ranunculus septentrionalis	1.026	13677	13330
Rudbeckia hirta (2)	0.863	16616	19311
Rumex Acetosella (2)	0.531	8273	15596
Rumex crispus (2)	0.657	17085	25976
Rumex hastatulus	0.563	11883	21106
Rumex obtusifolius (3)	0.706	15227	21602
Saponaria officinalis	0.970	9780	10082
Scirpus polyphyllus	0.894	16968	18991
Scrophularia leporella (2)	0.834	14553	17541
Sedum purpureum (2)	0.471	4061	8707
Sericocarpus asteroides (4)	0.703	12302	17549
Silene latifolia	0.872	21469	24620
Sinapis arvensis	0.888	18264	20567
Sisymbrium Nasturtium-aquaticum (2)	0.652	17274	26513
Sisymbrium sp.	0.803	18960	23611
Solidago altissima	0.959	15423	16090
Sol dago bicolor	0.815	14231	17461
Solidago juncea (3)	1.074	14710	13781
Solidago odora	0.911	15546	17064
Solidago rugosa	1.126	13037	11580
Solidago sp.	0.984	15483	15734
Spathyema foetida (2)	1.039	16424	15871
Specularia perfoliata	0.792	14756	18631
Tanacetum vulgare (2)	0.972	16164	16645
Thalictrum dioicum	0.988	14233	14406
Tovara virginiana (2)	0.451	9703	21991
Tridentalis americana	0.844	12471	14776
Trientalis borealis (2)	0.899	12194	13679
Trifolium agrarium	0.949	8323	8770
Trillium cernuum (2)	1.022	18054	17748
Unifolium canadense (4)	1.002	11655	11650

TABLE IV (*Continued*)

Constants for Herbs (*continued*)

	Δ	$\kappa \times 10^6$	$\kappa/\Delta \times 10^6$
Urtica gracilis	1.175	17213	14656
• Uvularia perfoliata	0.833	12372	14852
Vagnera racemosa (8)	1.041	12313	11880
Veratrum viride (2)	0.845	14073	16751
Verbascum Blattaria	0.812	13512	16640
Verbena urticifolia (5)	0.831	12651	15342
Veronica officinalis (2)	0.929	13730	14767
Vicia Cracca	0.875	12225	13971
V ola cucullata (2)	0.715	10030	14234
Viola pa'lens	0.763	12225	16022
Washingtonia longistylis	1.123	19195	17092
Xanthoxalis corniculata	0.796	21469	26971

Expressing the differences in percentages of the constants for ligneous forms, we note that the value for trees and shrubs is 30.46 percent higher than that of herbaceous plants.

These results are, therefore, in excellent agreement with those found in the Arizona deserts and in the Jamaican rain forest.

The constants set forth in Table VI show that the specific electrical conductivity for shrubs is slightly lower than that for trees. The difference is, however, smaller than its probable error. The differences between the conductivities of the leaf tissue fluids of trees and herbs, shrubs and herbs, and all ligneous species and herbs, are several times as large as their probable errors and show that the conductivity is distinctly higher in herbaceous than in ligneous plants.

The constants for the ratio of electrical conductivity to freezing point lowering, κ/Δ, appear in Table VII.

The entries in this table show that the ratio of conductivity to freezing point lowering is lower in trees than in shrubs, although the difference cannot be considered significant in comparison with its probable error. The ratio of conductivity to freezing point depression is much smaller in both trees and shrubs than it is in herbs. The ratios ($\times 10^6$) are

TABLE V

Statistical Constants for Freezing Point Lowering, Δ

	Mean	Standard deviation	Coefficient of variation
(1) Trees, N = 19	1.2921 ± 0.0429	0.2772 ± 0.0303	21.46 ± 2.45
(2) Shrubs, N = 36	1.1775 ± 0.0244	0.2174 ± 0.0173	18.46 ± 1.52
Difference (1) — (2)	+0.1146 ± 0.0493	+0.0598 ± 0.0348	+3.00 ± 2.88
(1 + 2) Trees and shrubs, N = 55	1.2171 ± 0.0224	0.2459 ± 0.0158	20.20 ± 1.35
(3) Herbs, N = 162	0.8464 ± 0.0105	0.1986 ± 0.0074	23.46 ± 0.93
Difference (1) — (3)	+0.4457 ± 0.0441	+0.0786 ± 0.0311	—2.00 ± 2.62
Difference (2) — (3)	+0.3311 ± 0.0265	+0.0188 ± 0.0188	—5.00 ± 1.78
Difference (1 + 2) — (3)	+0.3707 ± 0.0247	+0.0473 ± 0.0174	—3.26 ± 1.64

TABLE VI

Statistical Constants for Specific Electrical Conductivity, $\kappa \times 10^6$

	Mean	Standard deviation	Coefficient of variation
(1) Trees, N = 19	11213 ± 494	3195 ± 350	28.49 ± 3.36
(2) Shrubs, N = 36	10770 ± 339	3019 ± 240	28.03 ± 2.40
Difference (1) — (2)	+443 ± 599	+176 ± 425	+0.46 ± 4.13
(1 + 2) Trees and shrubs, N = 55	10923 ± 281	3088 ± 199	28.27 ± 1.96
(3) Herbs, N = 162	14308 ± 192	3624 ± 136	25.33 ± 1.01
Difference (1) — (3)	—3095 ± 530	—429 ± 375	+3.16 ± 3.51
Difference (2) — (3)	—3538 ± 389	—605 ± 275	+2.70 ± 2.60
Difference (1 + 2) — (3)	—3385 ± 240	—536 ± 240	+2.94 ± 2.20

TABLE VII

Statistical Constants for Ratio of Specific Electrical Conductivity to Freezing Point Lowering, $\kappa/\Delta \times 10^6$

	Mean	Standard deviation	Coefficient of variation
(1) Trees, N = 19	9092 ± 462	2987 ± 327	32.85 ± 3.96
(2) Shrubs, N = 36	9529 ± 372	3312 ± 263	34.75 ± 3.07
Difference (1) — (2)	—437 ± 593	—325 ± 419	—1.90 ± 5.01
(1 + 2) Trees and shrubs, N = 55	9378 ± 292	3210 ± 206	34.23 ± 2.44
(3) Herbs, N = 162	17674 ± 282	5326 ± 200	30.13 ± 1.22
Difference (1) — (3)	—8582 ± 541	—2339 ± 383	+2.72 ± 4.14
Difference (2) — (3)	—8145 ± 466	—2014 ± 330	+4.62 ± 3.31
Difference (1 + 2) — (3)	—8296 ± 405	—2116 ± 287	+4.10 ± 2.73

9092 : 17674 in the case of trees and herbs and 9529 : 17674 in the case of shrubs and herbs. Since the ratio does not differ significantly in trees and shrubs it is quite proper to combine them. The average value of $\kappa/\Delta \times 10^6$ in all ligneous plants is 9378 ± 292 as compared with 17674 ± 282 in herbs. Thus the ratio κ/Δ is about 90 percent higher in herbaceous than in ligneous plants.

It seems desirable from the physiological side to determine whether conductivity or osmotic concentration is more nearly a constant for the species of a region. Furthermore, it is of interest to determine whether either of the three physico-chemical constants considered is significantly more variable in one class of plants (trees, shrubs, or herbs) than another.

Comparison of the variability of electrical conductivity and of osmotic pressure can only be made by means of the relative variation constants. The differences in the coefficients of variation of κ and Δ for the three growth forms are given in Table VIII.

TABLE VIII

Difference in Coefficients of Variation of Electrical Conductivity and Freezing Point Lowering

Growth form	Difference C. V.$_\kappa$ — C. V.$_\Delta$
Trees	7.03 ± 4.16
Shrubs	9.57 ± 2.84
Trees and Shrubs	8.07 ± 2.38
Herbs	1.87 ± 1.36

The comparison shows that for each of the growth forms investigated the variability of electrical conductivity from species to species is greater than that of osmotic concentration. The differences are conspicuously greater in ligneous plants (in which the conductivity is on the average small as compared with the osmotic concentration) than in herbaceous species in which the electrical conductivity is both absolutely and relatively much larger. As a matter of fact, the varia-

bility of κ and of Δ cannot be asserted to be significantly different in herbaceous species.

Turning to the question of the relative variability of the physico-chemical constants in the different growth forms we note that the variability of the freezing point lowering of trees is numerically greater than that of shrubs as measured by both standard deviation and coefficient of variation. The difference in the variability of the two groups of ligneous forms is not, however, sufficiently large to be considered significant in comparison with its probable error. The standard deviation of Δ in herbaceous forms is lower than that in either trees or shrubs. The average osmotic concentrations, as measured by Δ, is also lower in these forms. In consequence the relative variability as measured by the coefficient of variation is higher in herbaceous species.

The variability from species to species of the electrical conductivity does not differ, as far as the data now available show, in the two groups of ligneous plants. The standard deviations of the conductivities of herbaceous plants are higher than those of ligneous species, but since the average conductivities are also higher, their relative variabilities as measured by the coefficient of variation are somewhat lower.

Finally, the results of the ratio κ/Δ show that the standard deviations are far higher in herbaceous than in ligneous plants. The mean value of the ratio is also far higher, and as a result the coefficients of variation of ligneous species are higher.

Taking the results for variability as a whole, they seem to indicate that there is little difference between ligneous and herbaceous forms.

The foregoing results show clearly that the osmotic concentration is higher while the electrical conductivity is lower in the tissue fluids of ligneous than in those of herbaceous species.

The results for freezing point lowering are drawn from three climatically highly dissimilar regions. While those for electrical conductivity are based on determinations from one region only, they represent two years work.

TABLE IX

Average Value of $\kappa \times 10^6$ and of $\kappa/\Delta \times 10^6$ for Species Classified according to Osmotic Concentration

Δ	Mean value of $\kappa \times 10^6$				Mean value of $\kappa/\Delta \times 10^6$			
	Trees	Shrubs	Trees and shrubs	Herbs	Trees	Shrubs	Trees and shrubs	Herbs
0.465	—	—	—	9752	—	—	—	21094
0.558	—	—	—	12940	—	—	—	22619
0.651	—	—	—	14785	—	—	—	22990
0.744	10398	11075	10737	14234	14401	14119	14260	19237
0.837	—	11651	11651	14841	—	13877	13877	17975
0.930	6657	10243	9525	15506	7463	10994	10288	16689
1.023	14364	11795	12224	13352	14337	11460	11939	13190
1.116	9693	11245	10624	13919	9146	10115	9728	12439
1.209	12866	9804	10824	15772	10644	8125	8964	13357
1.302	—	11109	11109	—	—	8654	8654	—
1.395	8990	7943	8466	14355	6553	5749	6151	10234
1.488	13929	18084	14760	—	9280	12104	9845	—
1.581	—	8534	8534	17233	—	5432	5432	11121
1.674	12518	11979	12249	—	7568	7286	7427	—
[illegible]	[illegible]	—	[illegible]	—	[illegible]	—	[illegible]	—

TABLE X

Average Value of Δ and $\kappa/\Delta \times 10^6$ for Species Classified according to Specific Electrical Conductivity

$\kappa \times 10^6$	Mean value of Δ				Mean value of $\kappa/\Delta \times 10^6$			
	Trees	Shrubs	Trees and shrubs	Herbs	Trees	Shrubs	Trees and shrubs	Herbs
4000	—	—	—	0.471	—	—	—	8707
5000	—	—	—	—	—	—	—	—
6000	1.071	1.292	1.218	0.984	5702	4563	4942	6452
7000	1.012	1.124	1.068	1.035	7394	6441	6918	7067
8000	1.754	1.170	1.286	0.842	4659	7365	6824	10297
9000	1.377	1.315	1.332	0.841	6553	7031	6894	11210
10000	1.251	1.154	1.178	0.825	9994	8754	9064	13630
11000	1.312	1.059	1.143	0.868	8502	10958	10139	13444
12000	1.299	1.211	1.236	0.798	9484	10369	10116	16303
13000	1.655	1.057	1.356	0.791	7568	12429	9999	17254
14000	1.056	—	1.056	0.804	13469	—	13469	17593
15000	—	—	—	0.861	—	—	—	17747
16000	1.480	1.181	1.280	0.862	10504	13562	12542	20036
17000	1.333	1.017	1.174	0.814	12516	17323	14919	21658
18000	—	1.514	1.514	0.837	—	12104	12104	22167
19000	—	—	—	1.063	—	—	—	18904
20000	—	—	—	0.912	—	—	—	22663
21000	—	—	—	0 848	—	—	—	25120
22000	—	—	—	0.807	—	—	—	27571
23000	—	—	—	—	—	—	—	—
24000	—	—	—	0.991	—	—	—	24272
25000	—	—	—	—	—	—	—	—
26000	—	—	—	—	—	—	—	—
27000	—	—	—	0.936	—	—	—	28680

While the materials are rather too meagre for exhaustive statistical analysis they have been classified according to the magnitude of Δ and the average value of κ and of κ/Δ for each class of Δ has been determined. The results are presented in Tables IX and X.[1]

Diagram 1, which shows by the position of the two means

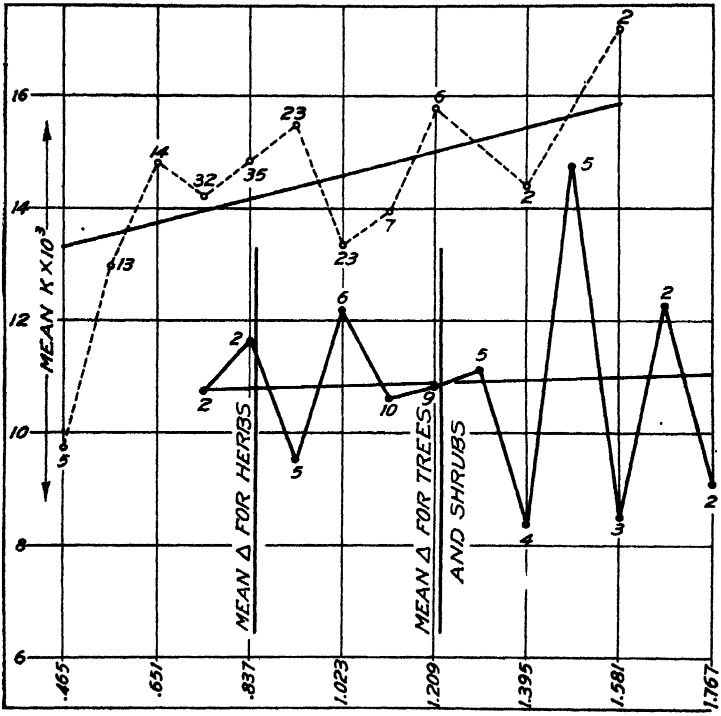

Diagram 1
Average values of specific electrical conductivity, κ, of leaf tissue fluids of ligneous and herbaceous species classified according to freezing point depression, Δ.

on the scale for Δ the conspicuous differentiation of ligneous and herbaceous plants for this constant, also brings out clearly the fact that for each grade of Δ the ligneous forms have a lower electrical conductivity than the herbaceous species. The mean values for κ for the two growth forms lie

[1] The class interval of Δ has been selected to represent 5 percent of the molecular lowering taken as $\Delta = 1.86$.

at the points where the straight lines fitted to the means intersect the verticals representing the mean values of the freezing point lowering.

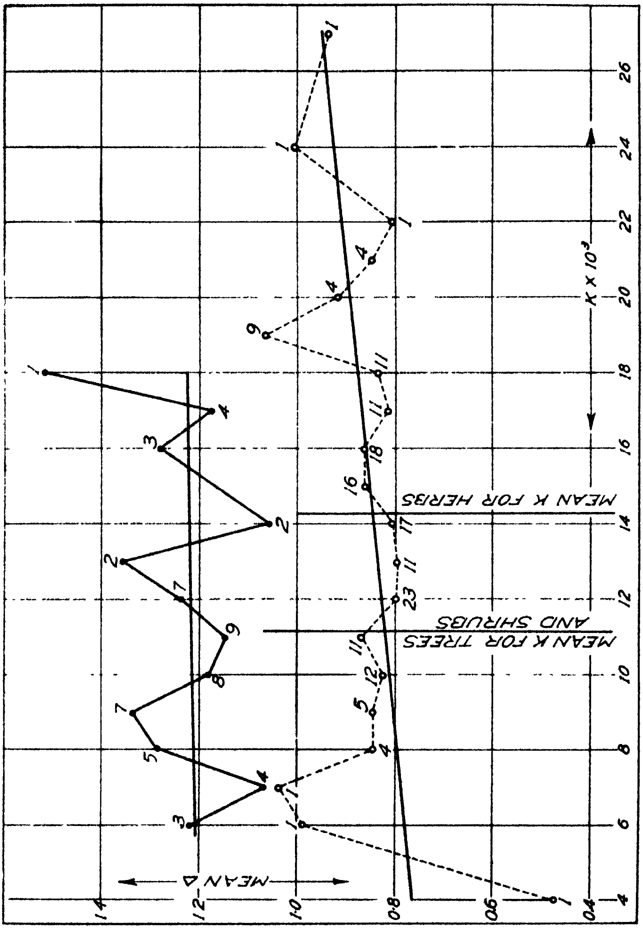

Diagram 2

Average osmotic concentration, in terms of freezing point lowering, of leaf tissue fluids of ligneous and herbaceous species classified according to specific electrical conductivity, $\kappa \times 10^6$.

The mean values of Δ for various grades of κ are shown in Table X and represented graphically in Diagram 2. The differentiation of ligneous and herbaceous forms with respect

to both osmotic concentration and electrical conductivity is conspicuously shown, both for the series as a whole and for

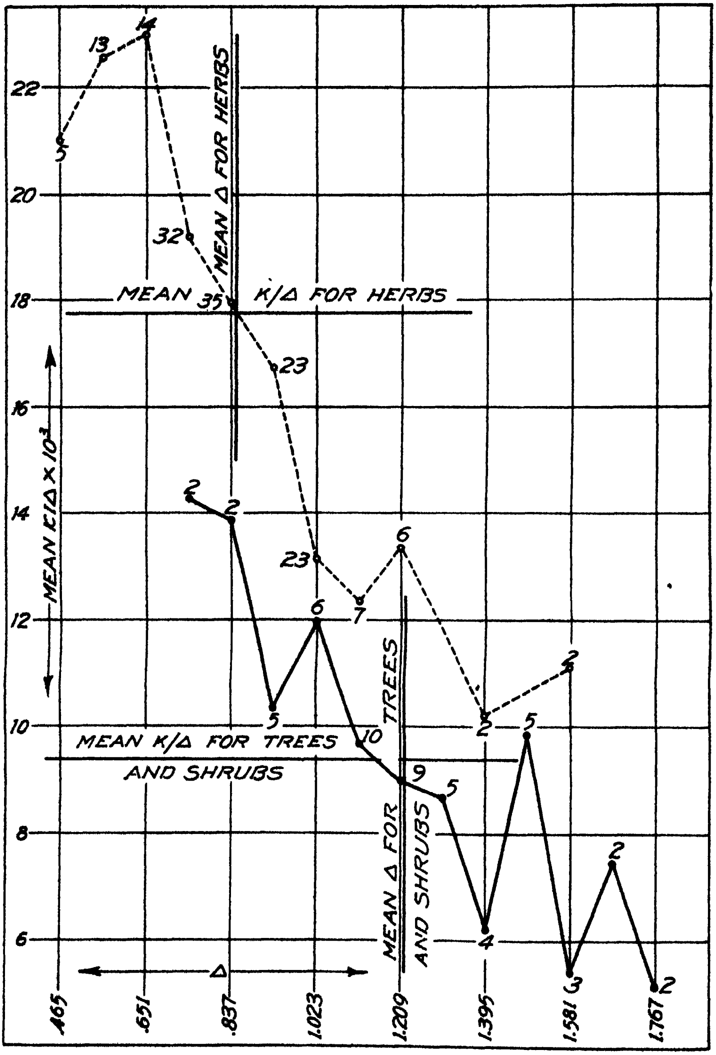

Diagram 3

Mean ratio of electrical conductivity to freezing point depression, κ/Δ, in leaf tissue fluids of ligneous and herbaceous species classified according to freezing point depression, Δ.

each of the groups classified with respect to the magnitude of their electrical conductivity.

The question will naturally arise as to whether for each grade of Δ or of κ ligneous plants have a lower ratio of κ to Δ than herbaceous species. The averages of κ/Δ for species with various freezing point depressions are given in the second section of Table IX and the results are represented graphically in Diagram 3. These show clearly that if the plant species of the vegetation investigated be classified according to the osmotic concentration (in terms of Δ) of their leaf tissue fluids, the leaf tissue fluids of the ligneous plants of each class show a lower ratio of κ to Δ than that found in the herbaceous species.

If the plant species are classified primarily by the value of κ as in Table X, the same result is obtained. The ratio of κ to Δ is lower for ligneous than for herbaceous species in each sub-class.

These diagrams fully substantiate the conclusions as to the differentiation of ligneous and herbaceous species with respect to the physico-chemical properties of their tissue fluids.

The conspicuous feature of Diagrams 1 and 2 is the very slight slope of the straight lines which smooth the rather irregular averages. These show that there is little relationship between the values of κ and of Δ in the two groups. Determining the correlation coefficients by the usual product moment method[1]

$$r_{\Delta\kappa} = \frac{\Sigma(\Delta\kappa) - \bar{\Delta}\bar{\kappa}}{\sigma_\Delta \sigma_\kappa}$$

where the bars denote means and the sigmas denote standard deviations, we have the following measures of relationship between the magnitudes of κ and Δ in the various series. The linear regression equations deduced from the formulae

$$\kappa = \left(\bar{\kappa} - r_{\Delta\kappa}\frac{\sigma_\kappa}{\sigma_\Delta}\bar{\Delta}\right) + r_{\Delta\kappa}\frac{\sigma_\kappa}{\sigma_\Delta}\Delta$$

$$\Delta = \left(\bar{\Delta} - r_{\Delta\kappa}\frac{\sigma_\Delta}{\sigma_\kappa}\bar{\kappa}\right) + r_{\Delta\kappa}\frac{\sigma_\Delta}{\sigma_\kappa}\kappa$$

are also given.

[1] J. Arthur Harris: Am. Nat., 14, 693–699 (1910). All moments upon which the means, standard deviations and correlations are based, are obtained directly from the protocols of data without grouping.

For trees:

$$r = +0.127 \pm 0.152, \quad \kappa \times 10^6 = 9322 + 1464\Delta$$

$$\Delta = 1.1685 + 0.00001102\,\kappa \times 10^6$$

For shrubs:

$$r = -0.079 \pm 0.112, \quad \kappa \times 10^6 = 12059 - 1095\Delta$$

$$\Delta = 1.2385 - 0.00000567\,\kappa \times 10^6$$

For trees and shrubs:

$$r = +0.022 \pm 0.091, \quad \kappa \times 10^6 = 10591 + 273\Delta$$

$$\Delta = 1.1985 + 0.00000153\,\kappa \times 10^6$$

For herbs:

$$r = +0.150 \pm 0.052, \quad \kappa \times 10^6 = 11997 + 2730\Delta$$

$$\Delta = 0.7293 + 0.00000819\,\kappa \times 10^6$$

The correlations between the freezing point lowering and the electrical conductivity of the sap of ligneous plants are of a very low order and statistically insignificant in comparison with their probable errors. The value for shrubs is actually negative in sign. That for trees and shrubs together is sensibly zero. The coefficient for herbaceous plants is also low, but may indicate a slight relationship between the two constants, higher values of Δ being associated with higher values of κ and *vice versa*.

These results show that, in the vegetation of the glacial moraines of Long Island at least, there is practically no relationship between the concentration of ionized electrolytes and of total solutes (molecules and ions) in the leaf tissue fluids.

If there be little relationship between the magnitudes of κ and Δ one might expect the value of the ratio κ/Δ to decrease as Δ becomes larger and to increase as κ increases in magnitude. This is shown in Diagrams 3 and 4 to be the case.

The explanation of the lower conductivity of the tissue fluids of ligneous plants presents a problem for future investigation.

It may be suggested that the arborescent forms are exposed to greater insolation, and in consequence show greater photosynthetic activity. A fragment of evidence in this

direction is furnished by the fact that Δ increases while the value κ/Δ decreases with height in arborescent plants.[1]

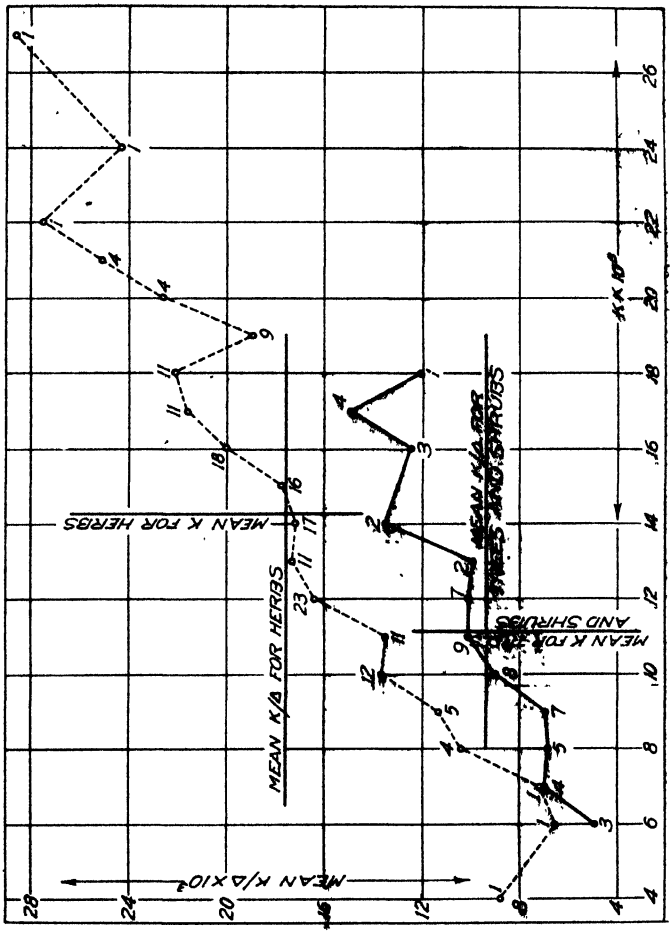

Diagram 4

Mean ratio of electrical conductivity to freezing point depression, κ/Δ, in leaf tissue fluids of ligneous and herbaceous species classified according to electrical conductivity, κ.

Summary

Studies in the Arizona deserts, in the Jamaican montane

[1] J. Arthur Harris, R. A. Gortner and John V. Lawrence: Bull. Torr. Bot. Club, 44, 267–286 (1917).

rain forest, and in the mesophytic habitats of the north shore of Long Island, have shown that the osmotic concentration, as measured by the cryoscopic method, is far higher in the leaf tissue fluids of ligneous than of herbaceous species.

A large series of determinations in the various non-halophytic habitats of the north shore of Long Island shows that the specific electrical conductivity of the expressed leaf tissue fluids of ligneous species is lower than that of herbaceous species. This shows that while the concentration of ionized electrolytes is lower in ligneous than in herbaceous forms, the reverse is true for total solutes.

Because of the wide geographic range and the great diversity of conditions (xerophytic, mesophytic and hygrophytic) under which the investigations on osmotic concentration were carried out, there can be no reasonable doubt but that the differentiation of ligneous and herbaceous plants with respect to the magnitude of their osmotic concentration (Δ) is a general biological law. Until confirmed by investigations in other regions presenting different conditions for plant growth[1] the results for conductivity cannot be asserted to be of universal validity.

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of Washington

[1] These investigations are now in progress.

A STUDY OF THE ABSORPTION SPECTRA OF POTASSIUM FERRO- AND FERRICYANIDES

BY FREDERICK H. GETMAN

The existence of an isomeric modification of ordinary potassium ferricyanide was discovered by Locke and Edwards[1] in 1899. By treating a solution of the ordinary red or α-potassium ferricyanide with a dilute acid and subsequently precipitating with alcohol, an olive-green salt was obtained which, on analysis, was found to correspond to the formula $K_3Fe(CN)_6.H_2O$.

This salt, known as potassium β-ferricyanide, differs in many of its reactions from the ordinary or α-salt. This is notably true of the reaction with bismuth nitrate with which the β-salt gives no precipitate while with the α-salt a copious yellow precipitate is obtained. The two salts have also been shown to differ in crystalline form.

Bellucci and Sabbatini[2] subsequently confirmed the statements of Locke and Edwards and furthermore suggested that the α- and β-ferricyanides may be regarded as nitrile and isonitrile forms.

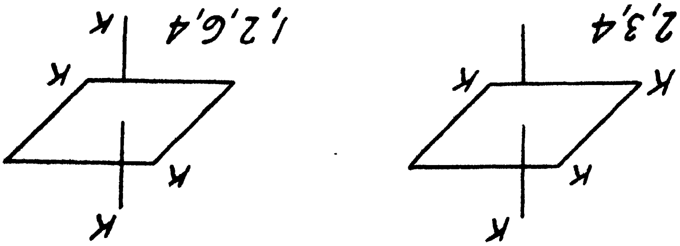
Hauser and Biesalski[3] attempted to show that potassium ferricyanide does not exhibit the phenomenon of isomerism as claimed by Locke and Edwards, but that the two salts are identical except for the presence of a minute trace of colloidal Prussian blue in the so-called β-modification. That the conclusions reached by Hauser and Biesalski were incorrect was clearly shown by Wells,[4] who repeated a portion of the work of Locke and Edwards and fully confirmed their statements.

Werner, in his "Neuere Anschauungen," treats the isomerism of the ferricyanides under the heading, "Unaufgeklärte Isomerieerscheinungen" and points out that this particular

[1] Am. Chem. Jour., 21, 193, 413 (1899).
[2] Atti. Accad. Lincei, 23 I, 176 (1911).
[3] Ber. deutsch. chem. Ges., 45, 3516 (1912).
[4] Am. Chem. Jour., 49, 205 (1913).

case demands further investigation before it will be possible to determine the specific character of the isomerism which it presents.

In 1911, Briggs[1] published a paper on the isomerism of the ferrocyanides in which he describes a series of experiments which led him to conclude that the ferrocyanides are also capable of existing in two isomeric modifications which bear the same relation to each other as the α- and β-ferricyanides of Locke and Edwards and which, in consequence, he termed the α- and β-ferrocyanides. The α-ferrocyanide of potassium, as obtained by Briggs, was pure white in color, whereas the β-ferrocyanide was cream-yellow. Aside from the difference in color, the α- and β-salts were found to differ in density, solubility and crystalline form. Their precipitation reactions were found to be much less distinctive than those of the α- and β-ferricyanides. Briggs concluded that the most probable explanation of the difference between his isomeric ferrocyanides was that they are stereoisomers having the following formulas:



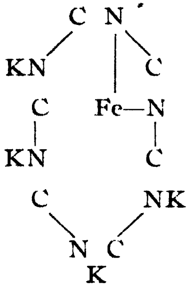
The isomerism of the α- and β-ferrocyanides of Briggs has been made the subject of an investigation by Bennett[2] who, from measurements of their crystal form, concludes that the pairs of salts described by Briggs are identical except for traces of impurities. He does not deny, however, the possibility of isomerism among the ferrocyanides.

The constitution of the ferro- and ferricyanides has been throughly discussed by Friend.[3] He reviews the different

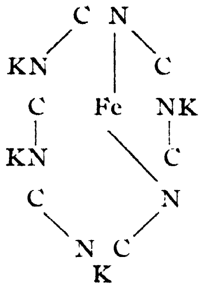
[1] Jour. Chem. Soc., **99**, 1019 (1911).
[2] Ibid., **111**, 490 (1917).
[3] Ibid., **109**, 718 (1916).

constitutional formulas which have been proposed from time to time from these compounds and, after having pointed out their various defects, he proposes a series of cyclic formulas which not only are consistent with the chemical behavior of the ferro- and ferri-cyanides but also offer a plausible explanation of their isomerism.

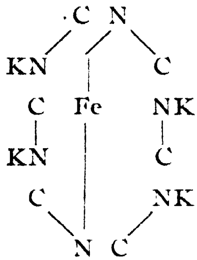
According to Friend, the following formulas are possible for potassium ferrocyanides:



Ortho- or 1:2 ferro-cyanide.



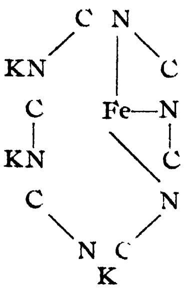
Meta- or 1:3-ferro-cyanide (α)



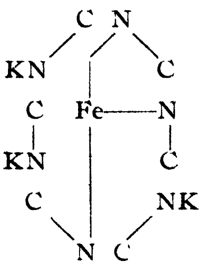
Para- or 1:4-ferro-cyanide (β)

It will be observed that the ortho-form in reality consists of the double salt, $4KCN.Fe(CN)_6$, which may reasonably be assumed to be unstable in view of the well-known instability of ferrous cyanide. From the fact that nitro-prussic acid is formed when nitric oxide is bubbled through an acidified solution of potassium ferrocyanide, Friend concludes that the meta-form corresponds to the α-ferrocyanide of Briggs and hence the para-form must correspond to the β-salt.

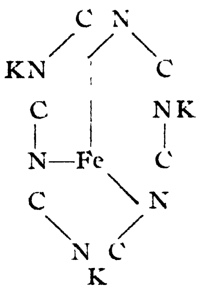
In a similar manner, Friend writes three cyclic formulas for potassium ferricyanide, as follows:



1:2:3-Ferricyanide.



1:2:4-Ferricyanide (β).



1:3:5-Ferricyanide (α).

Here again, the first formula represents an unstable compound while the other two are believed to correspond to the α- and β-ferricyanides of Locke and Edwards. Since the β-salt is stable in acid solution Friend concludes that it can be derived by oxidation from the β-ferrocyanide and, therefore, he attributes to it the 1 : 2 : 4 constitution.

In view of the conflicting opinions outlined above as to the existence of isomeric ferrocyanides and because of the relatively small amount of well-established data pertaining to the isomeric ferricyanides, it seemed of interest to study the ultra-violet absorption spectra of these substances in the hope that thereby some new light might be shed on the problem of their constitution.

Apparatus and Method

The well-known method of Hartley[1] and Baly[2] was followed in studying the absorption spectra of the ferro- and ferricyanides of potassium. A Hilger quartz spectrograph fitted with a wave-length scale, was used in making the spectrograms, and a condensed spark between electrodes of ferro-vanadium and chromium was employed as the source of ultra-violet light. A number of different combinations of metals were tried, but none proved as satisfactory as a ferro-vanadium alloy containing 25 percent vanadium against an electrode of chromium.

The spectrum obtained with this combination consists of a very large number of closely spaced lines, many of which are characterized by unusual brilliancy, especially in the extreme ultra-violet. So far as the writer is aware, this particular combination has not been used before in connection with the study of ultra-violet absorption spectra and he wishes to emphasize its superiority to any other that he has tried.

The solutions were examined in a "Baly tube" fitted with quartz ends and provided with a 10 cm scale graduated in millimeters. The thickness of the absorbing layer was at

[1] Proc. Roy. Soc., **33**, 1 (1882).
[2] Jour. Chem Soc., **39**, 153 (1881); **47**, 685 (1882).

first diminished by steps of 5 mm until complete transmission was secured, after which a second spectrogram was made in which the thickness of the absorbing column was diminished by steps of 2.5 mm over the region where sharper definition of the limits of absorption seemed desirable. The time of exposure was 10 seconds throughout the entire series of experiments.

Preparation of Materials

Potassium α-Ferrocyanide, $K_4Fe(CN)_6.3H_2O$. — Twenty-five grams of pure potassium ferrocyanide and 0.25 gram of potassium cyanide were dissolved in 100 cc of water and the solution transferred to a flask of such capacity that when tightly stoppered no air space remained over the surface of the liquid. After 24 hours the solution was filtered and alcohol added to the filtrate when a white crystalline precipitate of pure potassium α-ferrocyanide was obtained. The precipitate was washed thoroughly, first with alcohol and finally with ether, and then allowed to dry at room temperature.

Potassium β-Ferrocyanide, $K_4Fe(CN)_6.3H_2O$. Twenty-five grams of pure potassium ferrocyanide were dissolved in 100 cc of water and to the solution were added 2 5 cc of a solution of acetic acid containing 1 volume of glacial acetic acid in 10 volumes of water. The solution was allowed to stand for 24 hours, similar precautions being taken to avoid oxidation as in the preparation of the α-ferrocyanide. Alcohol was then added to the filtered solution and the pure potassium β-ferrocyanide was thrown down as a cream-colored crystalline precipitate. The precipitate was washed with alcohol until free from remaining traces of acid, and then, after washing with ether, was allowed to dry at room temperature.

Potassium α-Ferricyanide, $K_3Fe(CN)_6$. — According to Locke and Edwards,[1] the ordinary red potassium ferricyanide is the α-modification of the salt. A well-crystallized, chemically pure sample of the salt was obtained for the preparation of solutions of the α-salt as well as for the preparation of the β-ferricyanide.

[1] Am. Chem. Jour., 21, 193, 413 (1899).

Potassium β-Ferricyanide, $K_3Fe(CN)_6.H_2O$.—Fifty grams of potassium ferricyanide were dissolved in 100 cc of water and, after heating to boiling, 2.25 cc of concentrated hydrochloric acid (sp. gr. 1.19), diluted with three times its volume of water, were added to the mixture. The solution was placed on the water bath and, at frequent intervals, small portions were removed, allowed to cool, and then precipitated with 95 percent alcohol. Each precipitate was dissolved in water and the solution tested with bismuth nitrate; the formation of a precipitate indicated the presence of α-ferricyanide and hence, incomplete transformation into the β-ferricyanide. After 15 or 20 minutes, when complete transformation had been effected, the entire solution was allowed to cool and was then precipitated with alcohol. The precipitate so obtained was redissolved in water and again precipitated with alcohol. After washing with alcohol and ether, the precipitate was first allowed to dry in the air and then was placed in a vacuum desiccator where, after several days, the drying was complete.

In the preparation of all of the solutions conductivity water was used and care was taken to make the spectrograms immediately after the solutions were prepared. Solutions of the β-ferricyanide were tested with bismuth nitrate, both before and after exposure to the ultra-violet radiation in order to determine whether any reversion to the α-modification had taken place. In no case was any evidence of such reversion detected.

Experimental Results

The initial concentration of all solutions was 0.001 molar. It has been assumed that Beer's law holds for the ferro- and ferricyanides of potassium and therefore the change in absorption resulting from a reduction in the thickness of the absorbing column of a 0.001 molar solution from 10 cm to 1 cm will correspond to a ten-fold dilution. Each solution was diluted until complete transmission was secured. For convenience in plotting the curves of molecular vibration, the logarithms of the thicknesses in millimeters of a 0.0001 molar solution were plotted as ordinates against the reciprocals of the wave-

lengths (vibration frequencies) as abscissas. The curves of molecular vibration shown in Fig. 1 are plotted from the data given in Tables I, II and III.

TABLE I

Potassium Ferrocyanide

0.04224 gr $K_4Fe(CN)_6.3H_2O$ in 1000 cc of Solution

Thickness of Solution in mm	Oscillation Frequency			
50	4008	—	—	—
100	3808	—	—	—
150	3648	—	—	—
200	3550		—	—
250	3536	-	-	—
300	3495	—	-	—
350	3420	—	—	—
400	3367	—	3059	—
450	3367	3078	—	3030
500	3289	3096	—	3021
550	3289	3101	-	3017
600	3205	3115	—	3003
650	3205	3165	—	2985
700	3205	3185	—	2976
750	—	—	—	2976
800	—	—	—	2967
850	—	—	—	2958
900	-	-	—	2950
950	—	—	—	2941
1000	-	—	—	2933

It will be observed that the absorption spectra of the two ferrocyanides are identical, whereas a slight but well-defined difference between the spectra of the ferricyanides is clearly shown. Contrary to what might naturally be expected, there is marked dissimilarity between the absorption spectra of the ferro- and ferricyanides. This dissimilarity leads one to infer that a corresponding difference exists between the constitutional formulas of these two classes of compounds.

The identity of the absorption spectra of the two ferrocyanides described by Briggs furnishes additional evidence in

TABLE II

Potassium α-Ferricyanide

0.03292 Gr $K_3Fe(CN)_6$ in 1000 cc of Solution

Thickness of Solution in mm	Oscillation Frequency											
50	4361	—	—	—	—	—	—	—	—	—	—	—
75	4329	—	—	—	—	—	—	—	—	—	—	—
100	4292	—	—	3788	—	3279	3205	—	3086	3059	—	—
125	4273	—	3810	—	3781	3350	3205	—	3016	3021	—	—
150	4202	—	3810	—	3766	3484	3205	—	3145	3012	2439	2353
175	4202	—	3810	—	3759	3521	—	3195	—	3003	2439	2273
200	4202	—	3945	—	3759	3534	—	—	—	3003	2584	2273
225	4202	—	4011	—	3759	3617	—	—	—	3003	2584	2273
250	4202	—	4149	—	3738	3643	—	—	—	2976	2604	2222
275	—	4158	—	—	—	—	—	—	—	2967	2667	2222
300	—	—	—	—	—	—	—	—	—	2933	2667	2222
325	—	—	—	—	—	—	—	—	—	2933	2667	2222
350	—	—	—	—	—	—	—	—	—	2933	2667	2222
375	—	—	—	—	—	—	—	—	—	2801	2747	2198
400	—	—	—	—	—	—	—	—	—	2801	2770	2196
425	—	—	—	—	—	—	—	—	—	2801	2770	2188
450	—	—	—	—	—	—	—	—	—	2793	2770	2188
475	—	—	—	—	—	—	—	—	—	2793	2778	2188
500	—	—	—	—	—	—	—	—	—	2793	2778	2174

TABLE III

Potassium β-Ferricyanide

0.03472 Gr $K_3Fe(CN)_6.H_2O$ in 1000 cc of Solution

Thickness of Solution in mm	Oscillation Frequency												
50	4329	—	3788	—	—	—	—	—	—	—	—	—	—
75	4273	3795	—	3781	3279	3205	—	—	3078	—	—	—	—
100	4273	3802	—	3774	3279	3205	—	3086	—	3059	—	—	—
125	4273	3802	—	3774	3350	3205	—	3096	—	3059	—	—	—
150	4205	3817	—	3766	3496	3205	—	3195	—	3003	—	2439	2353
175	4202	3817	—	3766	3496	—	3205	—	—	3003	—	2439	2353
200	—	—	—	3656	3623	—	—	—	—	2985	—	2469	2273
225	—	—	—	3656	3636	—	—	—	—	2976	—	2591	2273
250	—	—	—	—	—	—	—	—	—	2933	—	2597	2222
275	—	—	—	—	—	—	—	—	—	2924	—	2652	2222
300	—	—	—	—	—	—	—	—	—	2924	—	2667	2222
325	—	—	—	—	—	—	—	—	—	2924	—	2667	2198
350	—	—	—	—	—	—	—	—	—	2793	—	2770	2174
375	—	—	—	—	—	—	—	—	—	2786	—	2770	2174
400	—	—	—	—	—	—	—	—	—	2786	—	2770	2174
425	—	—	—	—	—	—	—	—	—	2786	—	2770	2174
450	—	—	—	—	—	—	—	—	—	—	2786	—	2174
475	—	—	—	—	—	—	—	—	—	—	—	—	2174
500	—	—	—	—	—	—	—	—	—	—	—	—	2174

favor of the contention of Bennett that the two salts are essentially the same.

While the absorption spectra of the α- and β-ferricyanides are very similar, two of the absorption bands are appreciably more "persistent" than the corresponding bands of the β-ferricyanide. This fact may be taken as evidence in favor of the

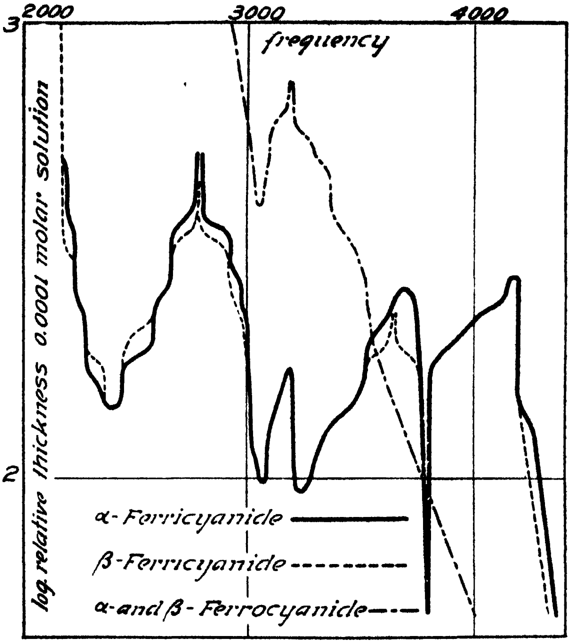


Fig. 1

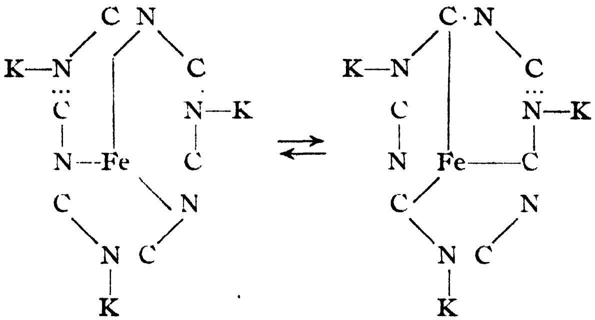
existence of two isomeric ferricyanides as claimed by Locke and Edwards.

In the light of existing formulas for the ferro- and ferricyanides of potassium it is difficult to account for the marked difference between their absorption spectra. According to the theory of Baly and Desch,[1] no organic substance shows an absorption band unless the possibility of tautomerism exists within the molecule. Since the phenomenon of

[1] Jour. Chem. Soc., 87, 768 (1905).

tautomerism involves a rearrangement of the linkages of the atoms within the molecule, it follows that vibrational disturbances must be set up among the attendant electrons and, according to Baly and Desch, it is to these electronic vibrations that the absorption bands are to be attributed. A large amount of experimental evidence has been adduced by Baly and Desch in support of their theory.

On the assumption that the existence of an absorption band implies a change of linkage accompanying the transition from one form to another, we find that the formulas proposed by Friend[1] for the ferro- and ferricyanides of potassium readily lend themselves to such rearrangement as is adequate to account for their respective absorption spectra. Thus, if we adopt Friend's formula for potassium α-ferricyanide, we may account for the presence of bands in its absorption spectra by assuming a condition of dynamic equilibrium such as is represented by the following scheme:



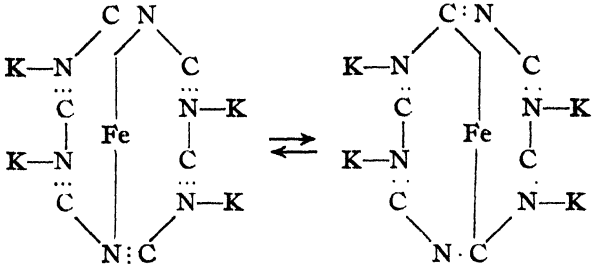
The absorption bands shown by the β-ferricyanide may be similarly accounted for by assuming a corresponding shifting of atomic linkages in the 1 : 2 : 4 formula of Friend.

In other words, the existence of absorption bands in the spectra of solutions of the α- and β-ferricyanides may be attributed to three possible changes of linkage in each of which the condition of equilibrium is represented by the scheme:

$$-\mathrm{C}\equiv\overset{|}{\mathrm{N}} \rightleftarrows \overset{|}{\mathrm{C}}=\mathrm{N}-$$

[1] Jour. Chem. Soc., **109**, 718 (1916).

If we assume a similar change of linkage to occur in the case of the ferrocyanides, it is apparent that the possible number of oscillating groups in the molecule will be reduced from three to two, as is shown below.



It is suggested that the marked difference in the absorption spectra of the ferro- and ferricyanides of potassium may be due to the difference in the manner and the relative positions of the potentially tautomeric groups within the molecules of each.

Summary

The salient points of this paper may be briefly summarized as follows:

(1) The absorption spectra of the α- and β-ferrocyanides of potassium described by Briggs have been shown to be identical. This fact may be taken as evidence in favor of the claim made by Bennett that these salts are not isomeric.

(2) A slight but well-defined difference between the absorption spectra of the α- and β-ferricyanides of potassium has been established, thus confirming the statement of Locke and Edwards that these salts are isomeric.

(3) A marked difference has been shown to exist between the absorption spectra of the ferro- and ferricyanides of potassium.

(4) On the assumption that the presence of an absorption band indicates a condition of potential tautomerism within the molecule, it has been shown that a modification of the structural formulas proposed by Friend for the ferro- and ferricyanides of potassium offers an opportunity for tauto-

meric change and hence affords a possible explanation of the presence of bands in their absorption spectra.

(5) Furthermore, it has been pointed out that the relative number and position of the tautomeric groups within the molecule may possibly be the cause of the marked difference between the absorption spectra of the ferro- and ferricyanides of potassium.

In conclusion, it is with pleasure that I acknowledge my indebtedness to Mr. Kenneth Tate, who has rendered able assistance in making the spectrograms.

Since writing the foregoing paper a second article by Briggs[1] has appeared in which the author summarizes the results of a series of experiments carried out in his laboratory to test the validity of the statement made by Bennett[2] that the so-called α- and β-ferrocyanides are identical

He furnishes considerable evidence to show that the salt which he originally called potassium β-ferrocyanide is in reality a mixture of ordinary ferrocyanide and aquopentacyanoferroate, the amount of the latter being far too small to admit of analytical detection.

Similarly he points out that the β-ferricyanide of Locke and Edwards probably consists of a mixture of ordinary ferricyanide and aquopentacyanoferriate.

When the ferricyanides are dissolved in water, partial decomposition occurs, as shown by the equation

$$K_3Fe(CN)_6 + H_2O \rightleftarrows K_2[Fe(CN)_5H_2O] + KCN.$$

The potassium cyanide formed furnishes cyanide ions which, owing to the slight degree of dissociation of the salt, are removed on the addition of a fairly strong acid. The velocity of the reaction is hence increased toward the right on the addition of an acid and toward the left on the addition of an alkali.

Potassium ferrocyanide also is believed to undergo hydrolysis when similarly treated as shown by the equation

$$K_4Fe(CN)_6 + H_2O \rightleftarrows K_3[Fe(CN)_5H_2O] + KCN.$$

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[1] Jour. Chem. Soc., 117, 1026 (1920).

[2] Loc. cit.

THE NATURE OF SECONDARY VALENCE[1]

BY HOMER W. SMITH

I. PRELIMINARY COMMUNICATION

1. The Concept of Secondary Valence

By secondary valence is meant that force which binds molecules together. Secondary valence is the chemist's name for the force which the physicists call cohesion. Apart from specific cohesion, we know very little about the intimate nature of this force; so little, in fact, that it cannot be said at the present time what part of the atom (or the molecule) is responsible for molecular aggregation.

Physicists who treat the problem of cohesion usually assume that the attraction of one molecule for another is to be attributed to "stray electric fields" surrounding the valence electrons of the atom; they further assume that molecular configuration plays an important part in determining the attraction between two molecules, and that the force acting between two molecules is subject to treatment on the basis of the inverse square, or the inverse fourth power, or some such mathematical function of the distance supposedly separating them. It is within the province of this paper to show that all three of these assumptions are erroneous. Evidence derived from a study of organic compounds will be presented to show that the forces acting between molecules are comparable to those forces in the atom which are responsible for atomic structure, in that they are rhythmic in nature and are consequently not subject to treatment under familiar electromagnetic laws.

Something of the general nature of secondary valence

[1] This is the first of a series of papers dealing with the nature of secondary valence and the rôle of molecular volume in the phenomena of solution. This investigation has been made in the Department of Physiology, School of Hygiene and Public Health, Johns Hopkins University, and it is submitted in accordance with the requirements for the degree of Doctor of Science in Public Health.

can be deduced from familiar facts. Since all substances may exist in the liquid or solid state, all atomic species must possess some secondary valence. The characteristic intensity of secondary valence associated with any molecular species, however, depends to a great extent upon the arrangement of the atoms in the molecule. This sensitivity to constitutive[1] relations concerns, from a causative point of view, only one or two atoms in the entire molecule. In other words, these variations in molecular activity are attributable solely to variations in the activity of one or two atoms, and they are the result of differences in the mode of chemical combination of these atoms. There are only a few atoms which are capable of varying in their activity in this manner. We shall be concerned in the present study only with oxygen and nitrogen, the two which are undoubtedly the most important.

Consider, for example, the compounds valeric acid and water. There certainly is no reason for believing that the molecules of these substances are held together by forces of a dissimilar nature; yet when we come to combine valeric acid with water, some writers go so far as to assume that an entirely new force enters into the intermolecular relations. Others are satisfied to proceed upon the basis that the valeric acid is not combined with the water at all, but that it is in an analogous state to a gas and occupying mythical intermolecular spaces for which there is no experimental justification. Apart from the results of this research, it seems a self-evident deduction that the valeric acid molecules have much the same relation to the solvent as do other molecules of water, and that the same forces are at work between them in identically the same manner.

Yet when we compare the solubility of valeric acid with

[1] The term *constitutive* should be carefully distinguished from *configurative*. When atoms are connected by primary valence to make a molecule, certain undefined interactions take place between them which alter their intrinsic nature. Such changes are called *constitutive* since they have to do with chemical *constitution*. The *configuration* of the molecule is a hypothetical feature with which the physical chemist will rarely have to deal.

that of pentane, we see that the introduction of two oxygen atoms has worked a great change in the properties of the latter, for while valeric acid is very soluble in water, pentane is almost insoluble. If now we pass to ethyl valerate, the solubility falls off again to a vanishingly small value. Here then is the problem of constitutive behavior: Two oxygen atoms in the carboxyl group can endow the pentane molecule with properties which render it very soluble in water; but the same oxygens in the ester are essentially as inert as the carbon and hydrogen themselves.

Under any concept of secondary valence, it must be admitted that the activity of one atom may vary through such wide extremes that this atom can practically determine the molecular behavior.

We have then, in résumé, a force possessed in some measure by all atoms. It may be possessed, however, by certain atoms under particular conditions, in great excess. In such atoms of variable activity, it is clear that the activity depends upon the mode of chemical combination. This is the force which we are now calling secondary valence.

Before we can make any progress in the analysis of the nature of secondary valence, we must introduce into all physical-chemical considerations another factor, namely, molecular volume. When a number of molecules come to positions of equilibrium with regard to electrical forces acting between them, there are obviously two factors brought into play. The first is the respective intensities of the attractions between them; the second is the relative amount of space which they occupy, or their respective molecular volumes.

Molecular volume has received little or no attention in the consideration of intermolecular relations. A study of various physical phenomena has convinced me that molecular volume is a determining factor in practically all the phenomena associated with liquids. By its use we have a means of correlating molecular behavior, and many relations are disclosed which otherwise would go unrecognized.

2. The Concept of Molecular Volume[1]

By molecular volume is meant the volume in cubic centimeters of a gram molecule of a particular substance, determined for certain practical reasons at the normal boiling point. Molecular volumes are additive in nature. That is, values may be obtained through the comparison of a series of compounds for each component atom and these atomic values may then be added together to derive the molecular volume of any desired molecular species. Constitutive variations are very much in evidence; for the volumes of some atoms, especially oxygen and nitrogen, vary by nearly 100 percent, according to the nature of their chemical union. But these constitutive influences are relatively few and constant and the results obtained justify the assumption that LeBas' methods of calculation are fundamentally sound.

We have in some measure been misled by the graphical formulas which we draw upon the blackboard into believing that molecules always have rigid and characteristic configurations. It is almost second nature to think of benzene as being ring-like and of hexane as being chain-like. Such a notion is immediately dispelled by a cursory inspection of molecular volume relations. The very application of the additive principle necessitates the immediate recognition of the fact that every molecule, no matter what its chemical nature, occupies a domain which is the perfect sum (admitting constitutive relations, which of course have to do with internal and not external matters) of the space occupied by the component atoms. This means that there is neither a "hole" inside benzene, nor any "cracks" nor "crevices" in hexane, as there would surely be were either of them composed of rigid spheres of carbon with smaller rigid spheres of hydrogen tacked on at various places. The principle of the perfect

[1] The molecular volumes used in this paper are either cited from LeBas or calculated according to LeBas' rules. (Gervaise LeBas: The Molecular Volumes of Liquid Chemical Compounds, Longmans, Green and Co, New York, 1915). A brief of LeBas' methods has been given in a previous communication. Jour. Phys. Chem., 24, 539 (1920).

sum implies that the six carbons and their attendant hydrogens make up a new domain which has the same *shape* as has each of the components, much as though we had put *several little spheres* together to make *one big sphere*. This rather surprising condition is initially a consequence, as I have said, of the additive nature of molecular volumes, but it is substantiated in an overwhelming manner by the rôle of molecular volume in the phenomena of molecular physics, where there is never any indication that any molecule has any other shape than that of a perfect sphere. That the shape of the molecular domain is not a perfect sphere in the literal sense is obvious from the same argument; for in that case there would be crevices between adjoining domains for which no allowance is made in the calculation of molecular volumes. We must rather look upon this shape as constantly varying between that of a tetrahedron and that of a sphere because of the constant agitation and collisions to which molecules of liquids are subjected. For the purposes of definition it should suffice to call it polyhedral, with the reservation that there can be no "dead" interstices between adjoining domains.

It is difficult to conceive of any atomic theory so mercurial as to explain satisfactorily the facts disclosed by a study of molecular volumes.

The atom is supposed to be a very porous affair, about as porous as the solar system. All physical experience shows us, however, that the space between the particles of electricity which compose the atom is so filled or constrained by lines of force that no two atoms can occupy the same space at the same time, or even overlap beyond certain assumed limits. Atoms thus held together by electrical forces constitute the molecule in which the atomic arrangement accounts for the chemical identity, which is never lost. We have just seen that the space relations of molecules are vastly different from what we would expect from the permanence of this atomic arrangement. The molecular volume at the boiling point is about three times what it is at absolute zero. This increase in volume is sometimes attributed to increased molecular

motion. The validity of this assumption is open to question, but even if we do assume that any part of the *molecular volume* in the liquid state (which, for the purposes of this paper, is synonymous with *molecular domain*) is due to molecular motion, this fraction must be statistically identical under like conditions for various molecular species. It thus becomes a universal factor which may be omitted from immediate consideration. To all intents and purposes the molecular domain is *completely filled* by the molecule. The boundary of the domain is purely an imaginary surface within which no other molecule can transgress. As to what the actual dimensions of the molecule may be, and as to the proportions of this actual volume and the volume of the apparent domain, we need not be concerned at the present time. The essential idea to be gained from an analysis of molecular volume relations is that *every molecule behaves as though it completely fills a definite space which has three-dimensional symmetry.*

Secondary valence, as has been said, is the force which binds molecules together. We must picture this union as being quite labile, for above the melting point there must be considerable molecular motion, crudely analogous to the motion of shot in a well-filled bucket which is being vigorously agitated.[1] *As a statistical result of this motion* and in keeping with the foregoing concept of molecular domains, we are entitled to think of secondary valence as acting as though it were either uniformly distributed over the surface of the molecular domain, or localized at its center. When molecular motion is restricted, as it must be at the interfaces of liquids, the molecule behaves as though its secondary valence were localized at one or more points. (It is noteworthy that here molecular volume relations fail, and the molecule assumes a definite

[1] Some molecular motion in liquids is a necessary assumption to account for vapor tension, solute diffusion and the absence of a structure. But a satisfactory explanation of all these could be based, it seems, just as well upon rotational motion as upon translational motion. If this motion is assumed to be largely rotational, it is evident that it would contribute but little to the molecular volume.

configuration or shape.) But there is no evidence to indicate that such a localization ever takes place when the molecule is completely and intimately surrounded by other molecules. In those molecules where two or more atoms actually contribute to the total secondary valence, the net result is apparently the same as though the entire secondary valence were to be attributed to one source.

3. Partition Coefficients

The phenomena of solution, from a practical point of view, are the most important phases of molecular behavior with which the physical chemist has to deal. Solubility relations are likewise the most susceptible to constitutive influences. On this basis, no better field could be chosen for the study of the nature of the forces acting between molecules. But a study of absolute solubilities is impractical because most of the lower members of chemically homologous series are miscible with water in all proportions, and hence they are excluded from direct consideration.

The problem may be approached, however, through a study of partition coefficients; for when a solute distributes itself between two immiscible liquids the amount in each of the liquids is an index of the relative solubility of the solute in the respective liquids. By determining the partition coefficients of a large number of compounds between any two immiscible liquids, such as water and xylene, it is possible to obtain an idea of the nature of the electrical forces involved in solution.

This method, though very simple and practical, presents several theoretical difficulties. For practical reasons we must work with titratable substances, using water as one solvent. These substances will undergo ionization in water and many of them will also be associated in the organic solvent. Since there is relatively no dissociation in organic solvents and no association in water, the ionized and associated fractions are removed from the system, so to speak, for neither can pass, as such, to the other liquid. In consequence, as smaller total

concentrations are used, both of these processes tend to lower the partition coefficient. In order to obtain a figure which is constant and characteristic of the solute, it is necessary to make a correction for these disturbing factors. Moreover, the second solvent may dissolve in the water and the water may dissolve in the second solvent, thus disturbing the normal distribution and the dissociation and association constants. In some cases a fifth disturbing factor is introduced in the formation of hydrates. After prolonged but vain attempts to establish a method of correction based upon stoichiometric equations and applicable to all cases, it was found necessary to adopt an empirical method of correction. This method will be discussed in more detail in a subsequent communication. The validity of the method can be established apart from the general results which it yields by the following facts:

(1) The partition coefficients of chemically related compounds between water and one solvent bear a constant ratio to the partition coefficients between water and a second solvent.

(2) The partition coefficients of two compounds bear a constant relation to each other regardless of the nature of the solute, the total concentration, or the nature of the second solvent.

(3) The partition coefficient of a compound may be derived independently of the relative amounts of water and second solvent used.

Conditions one and two are subject to certain well-defined exceptions which can only be treated in the discussion of the experimental work. From a consideration of the distribution law, it will be seen that these conditions are just what would be expected if all disturbing factors were eliminated; therefore they indicate that the method of correction is valid and that any relations disclosed by its use are, from a physical-chemical point of view, not open to question.

The partition coefficients of all the simpler acids and amines have been determined between water and xylene

and water and chloroform, and in a few cases between water and other solvents. The relations between these partition coefficients have been analyzed in terms of molecular volume. The principal facts disclosed by this analysis are as follows:

In any series of compounds having the same intrinsic intensity of secondary valence, the partition coefficient is a simple logarithmic function of the molecular volume.

Secondary valence is rhythmic in nature; that is, it varies in different molecular species by definite and related amounts. These differences in secondary valence are expressed in the partition coefficient by increases or decreases of constant arithmetric value. These variations in secondary valence are attributable to variations in the state of one or two particular atoms in the molecule and they have their origin in the mode of chemical combination. In all of the compounds studied, these rhythmic variations appear to be identical in nature; hence it is assumed that secondary valence is to be attributed to some part of the atom which is common and identical in its nature in all atomic species.

From the foregoing it can be seen that this atomic mechanism must function in a rhythmic fashion and that its activity is determined primarily by the mode of chemical combination.

The secondary valence associated with a given molecular species depends, however, not only upon its chemical nature, but also upon the nature of its environment. This fact, coupled with the fact that molecular volume is a determining factor in the relations of the solute to the solvent, shows that there are equilibrated intermolecular forces acting between the molecules of the solvent and the molecules of the solute, and that these intermolecular forces arise and are compensated in the underlying mechanism in those atoms of variable activity which are responsible for the characteristic secondary valence of the molecule.

Thus in such a compound as valeric acid, the mode of chemical combination of the (hydroxylic) oxygen determines the characteristic secondary valence of the molecule. When

such a molecule is placed in a dissimilar environment, such as water, a compensation between the external and internal forces must take place; this compensation is effected like all changes in the secondary valence of the molecule, by a change in the oxygen atom. Since this change involves some readjustment of the valence electrons, we can see in these facts a possible mechanistic cause for dissociation.

All these changes in secondary valence are rhythmic in nature presumably because they have their origin in some rhythmic mechanism in the atom analogous to the stable electronic orbits which have been postulated to account for Planck's quantum in energy radiation.

So far as I am aware, this is the first direct experimental demonstration of a quantum, or rhythmic variation, in the fundamental forces. The results are of interest not only in their relation to the nature of solution, but because they have a bearing upon the structure of the atom.

A detailed consideration of partition coefficients will be given in the next communication.

Baltimore, Md.

NEW BOOKS

Physics of the Air. *By W. J Humphreys. 24 × 16 cm; pp. xi + 665. Philadelphia: J. B. Lippincott Co., 1920. Price: $5.00.*—The subject is presented under four general headings· mechanics and thermodynamics of the atmosphere; atmospheric electricity and auroras; atmospheric optics; factors of climatic control. The titles of the chapters in the first section are: observations; some theoretical temperature relations of the atmosphere; observed vertical temperature gradients; the isothermal region or stratosphere; composition of the atmosphere; insolation; atmospheric circulation (4); winds adverse to aviation; barometric fluctuations; evaporation and condensation; fogs and clouds; the thunderstorm; lightning. In the second part there are only two chapters, one on atmospheric electricity and the other on the aurora polaris Under atmospheric optics the chapters are entitled: perspective phenomena; atmospheric refraction, refraction by water drops; refraction by ice crystals; reflection phenomena; diffraction phenomena; color of the sky; sky polarization. The subjects considered under factors of atmospheric control are: general summary; principal ice-age theories; vulcanism; other factors of climatic control.

Since cold air will settle to the bottom of a valley and since the temperature falls if one goes high enough, there should be a level of maximum temperature at some point in a mountain valley on a clear, still night. This is recognized by the mountain camper who pitches his tent above and not below his night fire, so as to avoid smoke, p. 117. The Swiss peasant builds his cottage on a knoll to keep above the valley flood of cold air, while the peach grower seeks the thermal belt to escape killing frosts.

It is evident that violent winds must often blow down steep slopes that separate high, snow-covered plateaus or mountain ranges from adjacent bodies of relatively warm water. Probably the best known of the violent fall winds is the bora of the northeast Adriatic, especially at Trieste, Fiume, and Zengg. The boras of these places, however, are not from the north as the name implies, but rather from the northeast and east-northeast.

"Another excellent example of this kind of wind occurs at Novorossisk, a Russian port on the northeast coast of the Black Sea where it blows down from a nearby pass in the mountains, occasionally with destructive violence. Probably, also, the brief but sudden and violent williwaws of steep, high latitude coasts have a similar origin.

"Another instance of convection due essentially to cooling is the well-known mistral, or dry, cold northerly wind of the Rhône Valley. Here the more or less persistent winter low over the warm waters of the Gulf of Lyons to the south and the frequent highs over the snow-covered plateaus of southeastern France to the north often coöperate in such manner as to produce extensive air drainage down the lower Rhône Valley. In general the cause of the mistral and its action are the same as those of the bora. It is less violent, however—its path less steep, and therefore itself not so distinctly an aerial cataract. Similar winds occur, of course, under like circumstances in other parts of the world, but the mistral is the best known of its class."

"Greenland, as is well known, is continuously covered with an enormous ice cap that rises to a gently rounded plateau of, roughly, from 2000 to 3000 metres (7000 to 10,000 feet) elevation. This plateau, whose crest runs approximately north and south, has been crossed several times—six in all—at as many different places, and in each case nearly constant down-slope or drainage winds of greater or less strength were experienced. Throughout its great area, therefore, Greenland is a region of almost perpetual aerial cascades and cataracts. The continuous refrigerative influence of its enormous ice cap, covering an area 18 times that of the State of Pennsylvania and rising at places to an elevation of over three kilometres (two miles), not only controls the direction and velocity of nearly all local winds, but obviously must be of decided influence on the general circulation of the middle and higher latitudes of the whole northern hemisphere—an important circumstance that will be taken up later.

"Antarctica, according to the reports of all its explorers, is quite as completely covered with ice as is Greenland, and it also rises, more or less domelike, to fully as great altitudes. Hence it would seem that its general effect on the movement of the air must be very similar to that of its great counterpart in the northern hemisphere—an inference now fully borne out by the many accounts and records of those who have skirted its coasts, crossed its plateaus, or wintered on its borders Sir Douglas Mawson, for instance, who spent many months during 1912-13 at Adelie Land, latitude 67° S., on the edge of the continent almost directly south of Tasmania, reports an average wind velocity for an entire year, from the interior toward the sea, of more than 22.4 metres per second (50 miles per hour). 'Day after day,' he says, 'the wind fluctuated between a gale and a hurricane' Velocities of 100 miles and over per hour occurred, and gusts of even much greater velocity occasionally were recorded."

On p. 213 we read: "Since the tornado rarely occurs in violent form except in that portion of the United States which is east of the Rocky Mountains, it follows that that combination of meteorological conditions essential to its genesis seldom obtains in other parts of the world. This combination appears to be very simple—only a vigorous convection between strong neighboring counter currents. But since vertical convection, as indicated by thunderstorms, is common enough in most parts of the world, it follows that the other factor—namely, strong counter currents—is the distinctly American phenomenon. That such currents should often occur east of the Rocky Mountains is obvious from the position and trend of these mountains themselves, giving rise to southward winds; and the location of the Gulf of Mexico, from which winds turn northward. No other similar combination of mountain and ocean wind controls exists, and therefore no other place has in all respects the same kinds, frequencies, and intensities of storms."

"Every aviator experiences in the course of his flights many abrupt drops and numerous more or less severe jolts. The cause of the first—the sudden drops—he has grouped together and called 'holes in the air,' while to the latter he has given such names as 'bumps,' 'dunts,' etc. There are, of course, no holes, in the ordinary sense of the term, in the atmosphere—no vacuous regions—but at various places in the atmosphere there are, occasionally, conditions which, so far as flying is concerned, are very like unto holes. Neither is the air ever 'full of bumps' in the sense of spots of abnormal density, but it often is turbulent

in such manner as to render flying rough and uncomfortable. Both sets of atmospheric movements, those that produce appreciable drops and those that cause jolts, are indeed real; and the former, because of their general interest and practical importance, will be considered in some detail. The latter, being of little importance, will only be mentioned incidentally. Furthermore, there are no 'pockets of noxious gas.' No single gas, and no other likely mixture of gases, has at ordinary temperatures and pressures the same density as atmospheric air. Therefore, a pocket of foreign gas in the atmosphere would almost certainly bob up like a balloon, or sink like a stone in water."

The above are some of the things that fortunately do not exist. The following are some of the disturbances which do exist and which may be a source of danger, especially if encountered near the ground: air fountains; air sinks; air cataracts; cloud currents, aerial cascades, wind layers; wind billows; wind gusts; wind eddies; air torrents; and air breakers.

The author is not clear as to the cause of the so-called dark lightning, p. 379, and has evidently not read the reviewer's paper on the subject. There is an interesting paragraph on sheet lightning, p. 377. "When a distant thundercloud is observed at night one is quite certain to see in it beautiful illuminations appearing like great sheets of flame, that usually wander, flicker and glow in exactly the same manner as does streak lightning, often for well-nigh a whole second, and occasionally even longer. In the daytime and in full sunlight the phenomenon, when seen at all, appears like a sudden sheen that travels and spreads here and there over the surface of the cloud. Certainly in most cases, so far as definitely known in all cases, this is only reflection from the body of the cloud of streak lightning in other and invisible portions. Often a blurred, yellowish streak is seen through the thinner portions of the intervening cloud. Occasionally, too, the cloud is wholly cleared in places where, of course, the discharge is white and dazzling. Conceivably a brush or coronal discharge may take place from the upper surface of a thunderstorm cloud, but one would expect this to be either a faint continuous glow or else a momentary flash coincident with a discharge from the lower portion of the cloud to earth or to some other cloud. But, as already stated, only reflection is definitely known to be the cause of sheet lightning. Coronal effects seem occasionally possible, but that they ever are the cause of the phenomenon in question has never clearly been established and appears very doubtful It has often been asserted, too, that there is a radical difference between the spectra of streak and sheet lightning, but even this appears never to have been photographically, or otherwise definitely established."

"Since the electricity of the thunderstorm obviously is generated within the cumulus cloud and there mechanically separated into upper and lower layers it may not at first be clear how discharges can take place to earth at all. Of course, there will be some lines of force between the earth and each cloud charge, but these must be relatively few so long as the charges are equal and approximately superimposed and the resulting dielectric strain correspondingly feeble. However, as the upper charge is carried higher, and especially as it is drifted away from the lower by the winds into which it projects, the lines of force between cloud and earth become more and more numerous, and the strain progressively greater until suddenly relieved by the lightning's disruptive flash.

"It would seem, therefore, that a marked difference between the wind velocities at the upper and lower storm levels would be especially favorable to frequency of cloud-to-earth discharges. Hence one would infer that heat thunderstorms, since they occur only when the general winds are light, are less dangerous—less likely to be accompanied by cloud-to-earth lightning—than those (presumably every other type) in which the wind velocity increases more rapidly with elevation. And from this one would further infer that tropical thunderstorms, since they commonly belong to the heat variety, are less dangerous than storms of equal electrical intensity of middle and higher latitudes, where the other or cross-current varieties prevail."

"Clearly, too, for any given region the lower the cloud the greater the danger. Hence a high degree of humidity is favorable to a dangerous storm, partly because the clouds will form at a low level and partly because the precipitation, and probably therefore the electricity generated will be abundant. Hence, too, a winter thunderstorm, because of its generally lower clouds, is likely to be more dangerous than an equally heavy summer one. Finally, as already explained, cyclonic or other cross-current thunderstorms presumably are more dangerous than those due to local heating, and therefore the thunderstorm of middle latitudes is generally more dangerous than one of equal severity in the tropics."

The author states, p. 424, that in the aurora, the source of the most prominent line, the green one, is not known. "It has often been attributed to krypton, but other conspicuous krypton lines are absent. Besides, krypton is too heavy to exist at auroral heights in sufficient abundance to produce a spectrum of such brilliance." Apparently auroras are now believed to be due to streams of alpha particles in the upper atmosphere shot off by radioactive substances in the sun, p. 425. "The seeming convergence of the auroral rays on a point far short of the magnetic pole, towards which they actually do converge, is due to perspective. Similarly, their apparent divergence from the magnetic zenith, thus forming a corona, is also a phenomenon of perspective, for here one is looking out along a bundle or tube of rays that, following the lines of magnetic force, surround him in every direction. The rapid, upward pulses of light along these rays, however, are quite real, and due, presumably, to progressive electric discharges."

We usually consider a mirage as an interesting but not an especially disturbing phenomenon. General Maude reports officially that in the battle of April 11, 1917, in Mesopotamia, the fighting had to be suspended temporarily owing to a mirage, p. 454.

The author is not enthusiastic about Arrhenius' carbon dioxide theory of the glacial period. He points out, p. 567, that "either doubling or halving the present amount of carbon dioxide could alter but little the total amount of radiation actually absorbed by the atmosphere, and therefore, seemingly, could not change appreciably the average temperature of the earth, or be at all effective in the production of marked climatic changes."

On p. 623 there is a discussion of possible changes in the oceanic circulation and their effects on climatic. "Clearly, if the immense system of hot-water heating by which the temperature of the whole surface of the earth tends to become equalized should be greatly modified, say, by the opening of a valve

here or the closing of another there, correspondingly great climatic modifications surely would have to follow. And there are several, perhaps many, such valves that have been opened or closed, irregularly, and from time to time, since the beginning of geological records. One such valve now partially open, perhaps at one time closed and at another still wider open than at present, lies between South America and the Antarctic continent. Another, now but a little way open, is Bering Strait, which doubtless has greatly changed from one to another geologic age Still another, now wholly closed, but at one time probably wide open, is the Central American region between the Caribbean Sea and the Pacific Ocean. This particular valve, if now widely opened, would, on the one hand, obliterate the Gulf Stream proper and probably diminish the Antilles current, and, on the other, greatly increase the Japan Current; and, of course, in each case induce widespread and marked climatic changes. Yet another valve, now rather wide open, that merits special mention, a valve that may have suffered many changes and have undergone its latest opening only in recent times, geologically speaking, is found in that ridge which by way of Iceland and the Faroe Island connects Greenland with north Scotland.

"With this Greenland-Scotland valve closed and even with all the other valves, channels of flow and deflecting obstructions substantially as they now are, it is well-nigh certain that the Icelandic "low" would shift to some point between Greenland and Newfoundland; that Labrador and the Hudson Bay region would receive a greatly increased precipitation; that the Norwegian Sea would become largely, if not wholly, ice-covered; and, finally, that Norway and Sweden, since they have the same latitude as Greenland, would be swept by winds of practically Arctic temperature and, therefore, eventually would become, like Greenland itself, almost wholly ice-capped. Indeed, any decided change in either the average intensity or average position of the Icelandic "low," if continued for even a few weeks, seems to produce a marked influence on the weather of west and north Europe. In general, whenever the average position of this "low" during a winter month is considerably to the west of its normal place, as occasionally happens, the average temperature of north Europe is likely to be several degrees below normal. That is, the above conclusion that a permanent or age-long shift of the Icelandic "low" far to the west of its present position would lead to, or, at least, permit, the reglaciation of portions of north Europe appears to be abundantly supported by direct observation. Nor would these be all the profound climatic changes that probably, indeed well-nigh certainly, would follow the closing of the Greenland-Scotland valve; but they are sufficient, if granted, to indicate how vitally impoitant the direction and magnitude of the ocean currents are to our climates and to local glaciation.

"Doubtless many other valves have contributed their part in the control of the earth's great water circulation and the regulation of its climatic details, but it would be tedious to take all of them up individually, and for the present purpose unnecessary, since it is desired here only to make clear the fact that oceanic circulation is a vital factor in the production and control of many a local climate."

The book is an extremely interesting one and contains a number of quite remarkable cloud photographs. The reviewer would have liked to see more references to unsolved problems, such as Piazzi Smyth's blue sun, etc.; but it

must be admitted that those are not the things that interest most people There is a misprint of turbulent for turbid on p. 539. *Wilder D. Bancroft*

Margarine. *By William Clayton. 22 × 14 cm; pp. xi + 187. New York: Longmans, Green and Co., 1920. Price: $4.75.*—In the preface the author points out that this monograph is the first of its kind in any language and that it aims to give a succinct account of the modern processes of the manufacture of margarine. The titles of the chapters are: introduction; oils and fats used in margarine manufacture; edible hydrogenated oils; the examination of milk for use in margarine manufacture; the manufacture of margarine; the theory of emulsification; butter and renovated butter; analysis of butter and margarine, deterioration of butter and margarine in storage; lard compound, nutritional chemistry; denaturing of margarine.

On p. 4 the author says: "From the purely scientific side, four great advances are noteworthy in margarine technology. They are: (1) the use of commercial cultures of lactic acid organisms for souring the milk used in churning, and thus imparting a butter flavor to the finished product; such cultures were independently suggested by Storch and Weigmann in 1890; (2) the introduction of vegetable oils and fats leading to the so-called 'nuts and milk margarines,' being placed on the market about 1906. Warr and Wright in 1900 described a typical 'nuts and milk margarine,' (3) the introduction in recent years of hydrogenated oils, whereby a new and extensive source of raw (fatty) material is opened up to margarine manufacturers; (4) the use of artificial milk, made from vegetable oils and nuts, is a distinct advance, and margarine can now be made, in which a purely artificial milk is pasteurized, soured and emulsified, yielding a product quite equal to that made with the usual separated cow's milk."

"From the practical standpoint, the most striking improvements have been: (1) the use of a sheet, and later, of a spray, of ice-cold water, to solidify the margarine emulsion; (2) the employment of a brine-cooled rolling drum, notably that of Schou, whereby the emulsion is rapidly cooled out of contact with the cooling medium; (3) the introduction of a continuous emulsifier or churning apparatus effecting much economy in time and space. A notable example is the electric continuous churn of the Silkeborg Maskinfabrik Zeuthen and Larsen; (4) the use of butter-working tables, mills, drums, blenders, and other devices for rolling or kneading the margarine."

On p. 26, it is admitted frankly that the fat-soluble vitamine A is lacking. "Recent investigations on the nutritional chemistry of foods in general have shown that hydrogenated oils are totally deficient in a most important substance, known as the 'accessory food substance, fat-soluble A.' This substance which plays a profound *rôle* in animal nutrition, is apparently absent in vegetable oils and fats, and consequently in their hydrogenated products, and it seems to be destroyed during the hydrogenation of animal oils and fats."

"Despite this objection, it must be admitted that the introduction of hardened oils marks a distinct advance in margarine technology, and in the manufacture of lard substitutes. In the latter case, the absence of the 'fat-soluble A' in hardened oils is no immediate detriment, since natural lard itself is exceptional amongst animal fats in being wholly deficient in 'fat-soluble A.'

An abundant source of clean, wholesome and reliable raw material is now available in addition to the usual animal and vegetable oils and fats hitherto solely employed. In time, a simple margarine may be manufactured, consisting of a single highly refined edible oil hydrogenated to the desired butter constituency; the nutritive element of fat-soluble accessory food substance being introduced either by blending with butter already containing it, or by the addition of a synthetic 'fat-soluble A' resulting from biochemical research."

Consequently the author concludes, p. 138, that "the whole question seems to depend upon the adequately varied and balanced diet of the individual. Children should preferably be fed on butter, but adults, with their stronger digestive powers, may with absolute impunity replace butter by either oleo- or vegetable-margarine, provided they consume sufficient amounts of the vegetative green parts of plants, since these furnish an ample supply of all three vitamines."

On p. 36 we read, "In addition to margarines for table use, there are also special qualities made for bakers and confectioners The bakers' margarine has a low melting point and may be easily beaten into a creamy paste Instead of the highest grade arachis or cotton-seed oils, such oils as soya, kapok, wheat, maize, and second-class arachis and cotton-seed oils are employed; otherwise the formulae of *cake* margarines, as they are called, approximate to those intended for table use."

Margarine intended for use in pastry-making is a tough product of considerably higher melting point than the cake margarine Oleostearine is a frequent constituent and pastry margarines have recently been made which contained up to fifty percent of hydrogenated fish oil (melting at 50°). Though table margarine is always churned with milk, it is optional to do so with cake margarine and it is seldom the practice with pastry margarine.

The milk used in making margarine is pasteurized, cooled, and then inoculated with lactic acid bacteria, p. 46. "It has long been known that the flavor of butter is to a large extent determined by the type and degree of development of lactic acid organisms in the original cream. The most desirable organism was found to be *B. lactis acidi*, Leichmann, and after suggestions mainly by Storch and Weigmann in 1890, it became common practice to introduce a "pure culture" of such organisms into the cream to induce and control the desired ripening, and thus lead to a good flavor in the subsequent butter. Later such cultures were suggested for use in the making of oleomargarine and renovated butter, and today an essential feature of practically all grades of margarine is the aiding of the milk souring by inoculation with pure cultures of *B. lactis acidi*, Leichmann."

On p. 52 we read that "The preparation of the fatty portion of the margarine being completed, and the milk suitably ripened or soured, it is now necessary to mix the two together as intimately as possible. An emulsion is produced, and it is absolutely essential to make as perfect an emulsion as possible. This stage of the manufacturing process is of the first importance. The object of emulsification is to imitate the emulsion found in cream and milk, where fat globules have diameters ranging from 0.01 mm to 0.0016 mm and remain as discrete particles. The general theory involved in this operation is worthy of study, and is dealt with at length in the next chapter.

"Until recently most margarine factories depended on the 'margarine churn' for making the emulsion This churn (illustrated in Fig 6) is jacketed, allowing of temperature regulation by either introducing hot or cold water to the jacket. Milk is admitted to the churn, which is provided with suitable agitating devices, e g , rapidly revolving baffle plates, and when at the desired temperature, the liquid fatty constituents are slowly run in, constant agitation being maintained It is essential to pour the oils into the milk, not vice-versa. For a ton of the melted oils and fats, various quantities of milk may be used, depending on market conditions and the quality of margarine being made. A volume of 30 gallons of milk with 30 gallons of water is convenient, though the emulsion may be made in such proportions as to yield a final product containing about 16% of water This is a matter largely depending on the subsequent treatment of the emulsion "

"When emulsification is complete the temperature is reduced to between 25° C and 35° C, depending on the composition of the fatty portion, and the custard-like emulsion is run off for cooling The object of cooling is to 'fix' the equilibrium condition attained in the emulsion, whereby the desirable intimate and finely divided mixture is maintained in the solid state Any 'breaking' of the emulsion would lead to the formation of unemulsified fat, whereby the texture of the final product would be harmed A margarine possessing a smooth, butter-like texture can only result provided a perfect emulsion is attained, and this subsequently cooled as rapidly as possible "

"Although the old type of margarine churn leads to excellent results, it occupies much space and absorbs considerable power for driving Consequently several improved emulsifying machines have been devised, aiming at the *continuous* production of an emulsion This is a great advantage, since the machines occupy much less space, and do not need refilling in 1 or 2 ton batches, as did the older or bulk type of churn The principle underlying continuous churns is the simultaneous admission of the oils and the milk into a chamber, preferably thermo-regulated, where some suitable device ensures intimate mixing or emulsification "

The importance of emulsification is shown by the fact that the author has devoted a special chapter to the theory of emulsification The book will be interesting to many people and especially to colloid chemists

Wilder D Bancroft

The Airplane. *By Frederick Bedell. 23 × 15 cm; pp 257 New York: D. Van Nostrand Company, 1920. Price, $3 00*—This is an amplification of the preceding books on Airplane Characteristics (**22**, 653) and the Air Propeller The seven other chapters now added make the book present a well-rounded treatment of the airplane, covering the general principles of airplane flight in a manner that is simple and yet reasonably complete and accurate While this book can scarcely be classed as physical chemistry by the wildest stretch of the imagination, there are several things in the new chapters which are distinctly interesting. On p. 171 the ceiling is defined as the highest altitude the machine can attain. At the ceiling the surplus power is zero and horizontal flight is possible at one velocity only, the machine losing altitude at any other velocity. A heavy machine may have a ceiling of only a few thousand feet,

while light machines, built for high altitudes, may climb to 30,000 or 35,000 feet.

On p. 179 the author says: "On account of these structural advantages the biplane or triplane is most generally used, not only for large load-carrying machines but for speed machines as well. Compared with a monoplane, a multiplane machine may have a shorter chord as well as a lesser span; with a shorter chord there is less travel to the center of wing pressure and hence there is greater stability. On the other hand a monoplane gives more unobstructed vision to the pilot or observer and has a certain simplicity. Furthermore, for the same aspect ratio, a monoplane has a greater lift per unit area than a multiplane. This is due to the fact that the lift of multiplanes is diminished by the interference between planes, discussed in a following paragraph."

The question of the unbalanced thrust is discussed on p. 210. "When the center of thrust is below G (the center of gravity), an increase in thrust due to opening the throttle gives a positive moment that temporarily causes the machine to nose up; a decrease in thrust due to closing the throttle gives a negative moment that temporarily causes the machine to nose down. This is an aid to the pilot in maintaining the proper flying attitude. When power is cut off, the machine noses down and tends to assume the proper gliding angle; when normal power is again put on, the machine tends to resume its horizontal flight path and, when excess power is put on, the machine tends to climb. Aircraft can usually be designed so that thrust passes through G or a little below it; it should not be so far below that the tendency to nose up or down is too great.

"When thrust passes above G, excess thrust has a negative moment which tends to make the machine nose down when the throttle is opened and to nose up when the throttle is closed. This tendency, although temporary, is bad, for it requires decided elevator control on the part of the pilot to counteract it. Unless thus controlled, a machine may nose up and stall when power is cut off. The effect may be offset to a certain extent by the action of the propeller slip stream on a depressing tail. Placing the center of gravity below the thrust can usually be avoided, but becomes necessary in some types of machines, for example, in flying boats with heavy hulls and high thrust."

The problem of directional stability is also interesting, p. 228. "When an airplane swings off from its course, to left or right, it is said to turn or yaw. Directional stability is the stability that keeps the machine to its course, that is, it restores the machine to its course whenever it yaws. The vertical or yawing axis passes through the center of gravity of the machine, lies in the plane of symmetry, and is more or less perpendicular to the flight path."

"This stability is similar to that of a weathercock and depends upon having the center of the keel surface back of the yawing axis, thus insuring a restoring moment whenever the machine departs from its course. It is to be remembered that the keel surface is all the surface seen from the side, including structure as well as auxiliary keels or fins. In some machines enough directional stability is obtained by the keel surface of the body itself, but this is usually supplemented by the addition of a small keel or vertical stabilizer in the rear. If the keel center is too far aft, side gusts will cause the machine to yaw too much.

"A machine should fly straight on its flight path; but it will fail to do so and will proceed crab-fashion if there is unequal resistance on the two sides.

This might be caused by unequal incidence of the two wings, distorted surface or camber, lack of symmetry in the tail, wrong alignment of body or fin or anything that might act as a rudder, for example, the setting of struts or stream-line wires so as not to lie true in the line of flight—points to be looked at in 'tuning up' a machine."

Wilder D Bancroft

Application of Electrolysis in Chemical Industry. *By A. J. Hale Edited by Edward Thorpe 23 × 15 cm; pp. ix + 148. New York: Longmans, Green and Co., 1918. Price: $2 50.*- In addition to an introduction expounding briefly the principles of electrolysis, the chapters include· methods of generating the current; the electrolytic refining of metals, the electrolytic winning of metals, the electrolytic production of hydrogen and oxygen; the electrolysis of alkali chlorides; chlorine and caustic soda; the electrolysis of alkali chlorides; hypochlorites, chlorates, perchlorates; the production of inorganic compounds, the production of organic compounds.

In the preface the author makes the following remarks: "The scope and purpose of this volume are sufficiently indicated by its title Electrolysis now plays an important part in the processes of Chemical Industry, and the value of Electro-Chemistry is generally recognised

"It is hoped that this work will prove useful to all those who are associated in any way with Chemical Science, and that it may stimulate interest in a rapidly growing branch of Chemistry which is worthy of more serious attention "

In view of this expressed purpose, the reviewer, on reading the book itself, is obliged to confess to a feeling of disappointment There is at the present time a very real need of a concise descriptive work in English on applied electrolysis, to supplement the more elaborate text by Allmand. Such a work, however, should be more than a restatement of the status of applied electrolysis as it existed twenty or even ten years ago While antiquated and long-abandoned processes might well be described in connection with present-day practice, it is certainly desirable and necessary clearly to distinguish the former from the latter, at least so far as a careful survey of the literature makes this possible. It is in this respect that the book under review proves disappointing.

The discussion of copper extraction on page 57 may be taken to illustrate the reviewer's objections The Hoepfner and the Siemens-Halske processes are described in detail and nothing is said to prevent the reader from assuming that these processes are in use to-day. As a matter of fact, the present-day processes are not described at all, although elaborate descriptions are available in the recent literature. Again, on page 63, the old Salom process of obtaining lead from galena by electrolytic reduction is definitely stated to be in successful operation, while actually it has not been employed technically for at least ten years. On page 69 *et seq* the reviewer objects to the author's way of describing the inoperative sodium processes of Darling, Becker and Borchers. The section on the extraction of zinc is almost the only case where the subject has been brought reasonably down to date.

On the other hand, for the reader desiring a brief and readily understood survey of the general field of applied electrolysis, the book will probably serve a useful purpose. The style is clear and direct: were the necessary omissions and additions carried out, sub equent editions should prove distinctly satisfactory.

T. R Briggs

Catalysis and Its Industrial Application. *By E. Jobling. Second edition. 18 × 13 cm; pp. viii + 144. Philadelphia: P. Blakiston's Son and Co., 1920. Price, $2.75.*—The first edition was reviewed (**20**, 455). The new edition has been revised and enlarged. The revision has not brought the book strictly up to date. On pp. 9, 10, catalytic poisons are discussed as something mysterious and that is scarcely counterbalanced by the casual remark on p. 46 that a poison may prevent access of the reacting gases to the catalyst by producing a film on its surface. On p. 15 the reference should have been to the new edition of Miss Woker's book. The work of Parsons and Perley on ammonia oxidation is not referred to, nor is there any discussion of the very important relation between the ammonia synthesis and the ammonia-soda process. The beneficial action of ceria in the Welsbach mantle, p. 62, is pretty certainly not due to its catalytic function in promoting the combustion of coal gas. There is no reference on p. 95 to the production of maleic acid from benzene. In spite of these shortcomings, the book is an interesting one, giving a great deal of information in a compact form. *Wilder D. Bancroft*

College Textbook of Chemistry. *By William A. Noyes. 20 × 14 cm; pp. viii + 370. New York: Henry Holt and Co., 1919. Price: $2 00*— At the end of each chapter there is given a summary and a set of exercises. The summary is admirable but it is not quite clear for whom the exercises are intended. They are presumably meant for the student and yet on page 5 he is asked what elements occur in solder and what other substances beside salt are purified by crystallization, questions which the student cannot possibly answer.

It is interesting to see how impossible it is even for so experienced a writer to avoid all mistakes. On p. 201 acetylene is listed under endothermal compounds, which is right, and the next statement is that acetylene decomposes into carbon and hydrogen when heated. On p. 244 zinc is called electropositive and copper electronegative, which was right once, but which is not the prevailing custom nowadays The account of the lead storage battery is not particularly happy because stress is laid on bivalent oxygen anions instead of on the formation of plumbic sulphate. The reviewer cannot endorse the view, p. 248, that lead peroxide is the anhydride of plumbic acid. It is certainly not helpful to say "that lead dioxide is similar in formula to carbon dioxide and that plumbic acid decomposes into lead dioxide and water as carbonic acid, H_2CO_3, decomposes into carbon dioxide and water." The formula for metastannic acid, p. 246, is a bit questionable. On the other hand the reviewer found a statement, p. 254, which was interesting and new to him. "By bringing two pieces of hot iron together with borax between them, the film of oxide on the surface of each is dissolved and, on pounding, the red-hot surfaces of pure iron unite to form a perfect weld, the liquid borax being forced out from between them." *Wilder D. Bancroft*

THE SIZE FREQUENCY DISTRIBUTION OF PARTICLES OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS

BY E. P. WIGHTMAN AND S. E. SHEPPARD

I. Introductory Paper

COMMUNICATION NO. 103 FROM THE RESEARCH LABORATORY OF THE EASTMAN KODAK COMPANY

Although the existence of some relation between size of grains in a photographic emulsion and the sensitiveness of the emulsion was accepted early,[1] little or no attention appears to have been paid to the variation in grain size in one and the same emulsion or layer, as a factor in the photographic properties. Attention was first called to this by C. E. K. Mees,[2] in a paper on "The Physics of the Photographic Process." He considers that, "inasmuch as the emulsions are not homogeneous, but each emulsion will contain grains of all sizes, the sensitiveness will depend upon the distribution

[1] J. Gaedicke: Eder's Jahrbuch. Phot., p. 209 (1895); Eder's Handbuch Phot., **3**, 66 (1903).

A. P. H. Trivelli in 1911 (Zeit. wiss. Phot., **9**, 168), had considered a certain relationship to exist between the size of grains of silver halide and the energy absorption when light falls upon them. Liesegang (Phot. Korr., **47**, 468), in the same year, stated that size of grain is concurrent with sensitiveness and is limited by visible granularity of the negative. Koch and du Prel (Phys. Zeit., **17**, 536) in 1916 also made some important observations tending to show that the so-called coarse grained plates are not necessarily the most sensitive. Recently, Slade and Foy (Proc. Roy. Soc., **97A**, 181 (1920)) have made some careful spectrophotometric measurements of the absorption of light by silver bromide. Further, a very recent article by R. E. Slade and G. I. Higson (Proc. Roy. Soc., **98A**, 154 (1920)) deals with the action of light on a dilute emulsion, which was said to have grains of uniform size and was one layer thick. Others have likewise given thought to the questions of the size of grain and sensitiveness and of the absorption of light by the silver halides. A more complete bibliography of this subject will be presented in a forthcoming monograph on the photographic theory by A. P. H. Trivelli and S. E. Sheppard.

[2] C. E. K. Mees: Jour. Franklin Inst., **179**, 141 (1915).

of the different sizes of grains, as also will the shape of the plate curve, this plate curve being the relation between density and logarithmic exposure." Further, he states "the shape of this curve depends to a considerable extent on the distribution of the different sizes of grains in the emulsion. With a homogeneous emulsion we should have a simple curve with a short over and under exposure portion, as shown in Fig. 1, and by adjusting the sizes of grain so that there is a sufficient number of grains distributed around the mean, we can diminish the size of the under exposure position to obtain

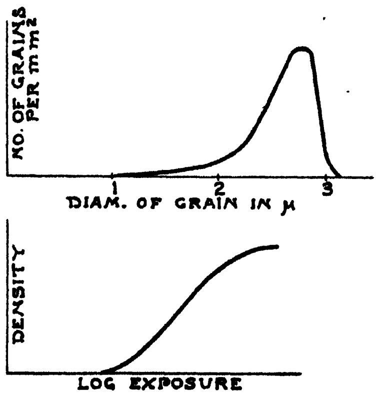

Fig. 1

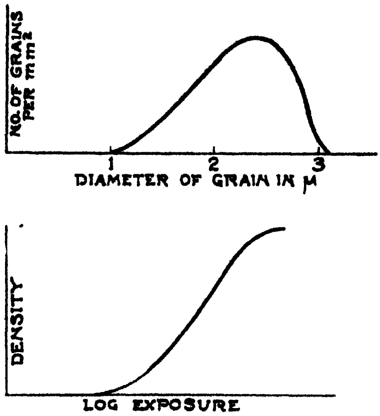

Fig. 2

a longer straight line (Fig. 2). We can therefore form a mental picture of the relation between the distributions of the grain and the sensitiveness curve." The author points out that up to that time there had been very little experimental work on this subject, and that the relations suggested were speculative. It appears that the main suggestion is that a proportionality exists between the degree of heterogeneity of the grains, otherwise the breadth of the frequency curve, and the latitude of the plate or emulsion. It is stated that any such considerations are to be regarded as limited to high speed emulsions.

In this connection we should point out that a first result of our experimental work is to show that the frequency curve alone is of less value in relation to the sensitometric curve than the projective area curve obtained by plotting the product of frequency by the projective area of grains of a given class against the corresponding classes. This will be discussed more fully later. It seems desirable, however, to call attention to this point at this stage.

Experimental investigation of the problem was begun in June, 1919, later papers give account of the results. Meanwhile there has appeared a paper by Slade and Higson,[1] and another by T. Svedberg,[2] in which the same problem is envisaged.

Slade and Higson state that "under ordinary conditions of exposure, the shape of the plate curve (as determined by Hurter and Driffield's method) is dependent on:

"(1) The relation of the different sizes of grains in the plate to each other and the quantity of each present.

"(2) The thickness and capacity of the film.

"(3) The time and method of development (though on 'infinite' development almost the same result is obtained whatever the developer and however much bromide it contains)."

They emphasize the importance of the first factor and show by H. and D. curves the difference between a plate with grains nearly of the same size and a plate with grains of mixed sizes. They also give photomicrographs which illustrate the two kinds of plates. The plates with grains of nearly uniform size have much steeper curves than those with mixed grains.

Their results are obviously only semi-quantitative, as no measurement of the dispersity of the silver halides is given. From the curves it appears that according to their view γ_∞ is increased by homogenizing the grain, and latitude, i. e., the projection of the straight line part of the plate curve, is

[1] R. E. Slade and G. I. Higson: Phot. Jour., **59,** 260 (1919).
[2] T. Svedberg: Zeit. wiss. Phot., **20,** 36 (1920).

diminished. In partial agreement with this is Lüppo-Cramer's[1] statement that plates of homogeneous grains, prepared by after-peptization of a finished emulsion, show a much earlier reversal period than plates with non-uniform grain.

In a quite recent paper by F. E. Ross,[2] of this Laboratory, on the relation between photographic density and exposure the author develops a new theoretical formula for the characteristic curve. It is pointed out that many formulae can be constructed depending upon particular assumptions of the following types:

a. Relative frequency of grains of varying size.

b. Relative sensitiveness of grains of varying size.

c. Variation of grain sensitiveness with light-intensity and wave-length for each class of grains.

d. Ratio of inert to active grains, depending on grain size.

e. Number of layers of silver halide.

f. Opacity of emulsion and its variation with wave-length.

The author points out that data for weighing these assumptions severally are lacking, hence, it is unprofitable to develop a formula on any but the simplest assumptions. As these he takes:

1. All grains in an emulsion are divisible into n groups, each group as a whole obeying the mass action law.[3]

2. The silver mass the same for each group.

3. The sensitivity factor of the groups arrayed in geometrical progression. This regards as equivalent true sensitivity difference (inherent) and apparent sensitivity differences (topical) due to thickness of emulsion. This equivalence is possible on account of the reciprocal equivalence of intensity and absorption-coefficient in a layer.

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[1] Lüppo-Cramer: Photographische Probleme, Halle, 1907.

[2] On the Relation between Photographic Density, Light Intensity and Exposure Time, by F. E. Ross: Jour. Optical Soc. America, 4, 255 (1920).

[3] That is, the law that rate of reaction is proportional to mass of material unchanged:

$$\frac{dx}{dt} = kI\,(A - x).$$

From these assumptions a formula is derived. Calling d_m the maximum density for infinite exposure (reversal neglected), k the sensitivity factor, R the common ratio of the sensitivities of the groups, the equation is obtained

$$D = d_m \left(1 - \frac{1}{n} \sum_{s=0}^{s=r-1} e^{-Rr^s It}\right.$$

Taking values $r = 1/2$ and $n = 1, 2, \ldots 10$ the field of practical emulsions should be well covered. A series of typical curves thus obtained are shown in the figure.

Now it will be noticed that for increasing values of n the slope, or γ_∞ becomes less and the straight line portion longer. Instead of the H. and D. latitude Ross takes the "range," as antilog of the projection of the line AA′ or BB′ (Fig. 3) on the exposure axis, as measure of the reproducing

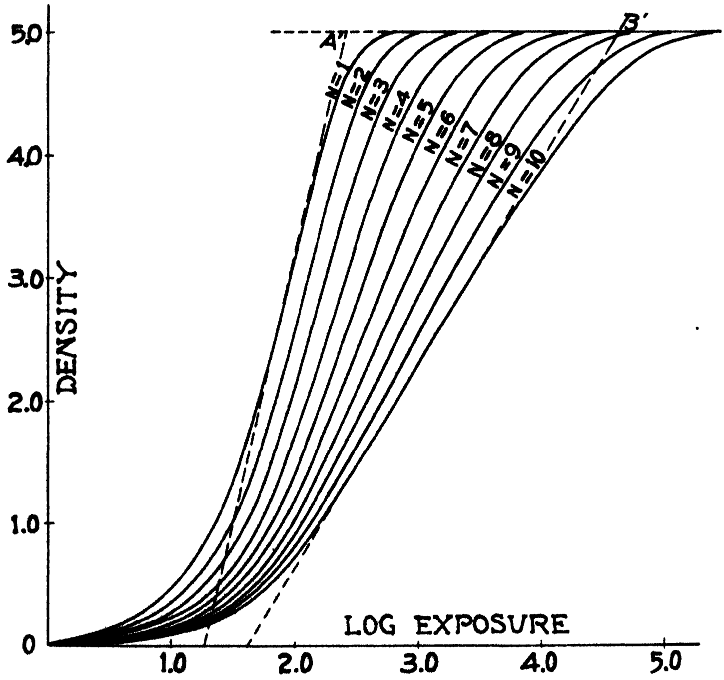

Fig. 3

power of an emulsion. The "range" increases with n as shown in following table:

n	Range
1	15
2	17
4	35
8	290
10	1000

Although n does not refer explicitly to the number of classes of different sizes, it would do so (*a*) if these had varying sensibilities (*b*) if opacities were constant. In this case, Ross' equation agrees partly with Mees' hypothesis that increasing grain heterogeneity increases latitude,[1] but also agrees with Higson and Slade's contention that more homogeneous grained emulsions have steeper curves.

We may point out here, anticipating certain results given in a later paper, that the influence of size of grains is not symmetrical in respect of their effect on exposure conditions (light intensity gradient) and development results (development factor). A great number of very small grains may contribute little on development to effective density, but they may very markedly affect the turbidity and opacity of the plate or film; hence their effect on the characteristic curve is not revealed by the density after development.

Slade and Higson were apparently ignorant of Mees' previous paper, and this is also the case with Svedberg. The latter considers that the problem at issue may be treated as, generally, relation of light sensitiveness to size of grain, and specifically, the four following cases of this:

(1) Every single grain has the characteristic curve of the plate.

(2) For every class of grains of nearly the same size in the emulsion there is a distinct curve.

[1] Latitude being analogous to Ross' range.

(3) The characteristic curve is only shown by emulsions with non-uniform grain.

(4) The relation between density and exposure expressed in the plate curve is a consequence of inhomogeneity of the photochemical illumination inside the photographic layer.

The last case is discounted largely by results with very thin layers previously obtained by Lüppo-Cramer and W. Scheffer,[1] and confirmed by Svedberg. As to the first case, Svedberg concludes, in agreement with Sheppard and Mees, that "reactivity" (rate of reduction) of the grain depends on exposure, but not absolute reducibility. Hence, the problem falls back on the second and third cases. It is pointed out that these require statistics of distribution of size in relation to exposure on ultimate development. Instead of measuring the reduced grains, of distorted appearance, Svedberg has applied the method of difference determination. Statistical measurements of grain size (or dispersity) are made first in the unexposed but developed emulsion, after treatment with a silver solvent, then they are made for a series of exposures. From these measurements two important diagrams are obtained, namely, (*a*) the curves connecting exposure and percentage reduced grains for each order of magnitude of the grains, (*b*) curves showing relation between size of grain and percentage made reducible after a certain exposure.

The first type of curve is comparable with the characteristic curve (since the number of grains is a factor in density). The second gives the relation of light sensitiveness to size of grain. The determination and division of sizes of residual grains was made by direct projection and microphotography of the exposed, developed layers of very thinly coated much diluted emulsion,[2] after dissolving of the developed grains. They were photographed at 1000 diameters, and then copied on paper at 4×, giving 4000× in all, and the mean *diameters* of circular grains were determined, and the projective areas of

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[1] W. Scheffer: Zeit. Elektrochemie., 14, 489 (1908).

[2] First should be determined the effect of dilution and thickness of coating on the plate curve.

the polyhedral grains were found by means of a millimeter network. All sizes were then reduced to projective areas, and divided into four classes of magnitudes.

The results are shown in the curves in Figs. 4 and 5.

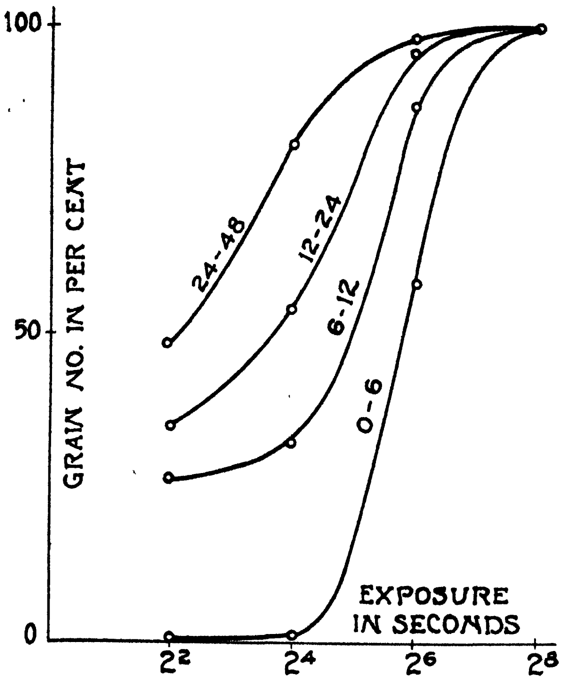

Fig. 4

From this it appears that every class of grains has its own characteristic curve; D, however, would be proportional to P_n, where n is the number of grains, P the photometric constant or factor. Now at present we do not know precisely the function $D = f(N, S)$, where $N =$ the number of grains per mm^3, $S =$ the magnitude. Assuming $D \propto N$, we have $D = Nf(S)$ and $f(S)$ remains to be determined. The only estimation we have of this at present is that of Higson,[1] who gives a relation between size of developed grain, and P, the photometric

[1] G. I. Higson: Phot. Jour., 60, 160 (1920).

constant. If we assume that the size of the developed grain, as a first approximation, is proportional to that of the original silver bromide grain, we can use Higson's values to calculate from Svedberg's data the actual D log E curves for his four classes of grains.

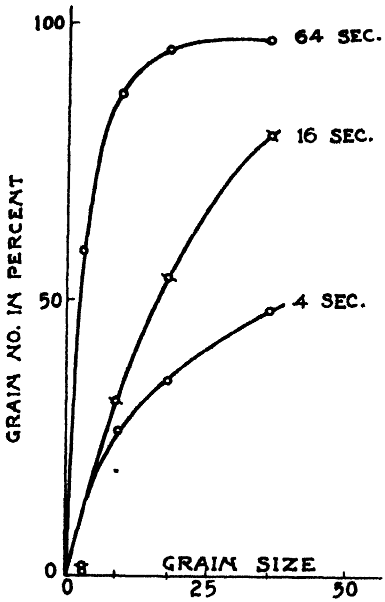

Fig 5

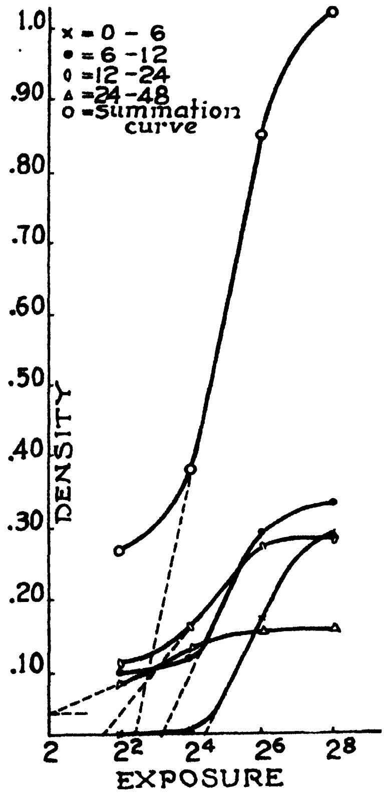

Fig 6

Table I gives the mean projective areas of the undeveloped grains for Svedberg's four classes and also these areas multiplied by four.[1] The corresponding diameters and photometric constants calculated from these are likewise given.

[1] According to Higson the developed silver grain is larger than the original bromide particle by this amount.

TABLE I

Mean Projective Areas of Undeveloped Grains in mm² $\times$ 16×10^4 Svedberg	Mean Projective Areas Undeveloped Grains in cm² = 4A	Mean Projective Areas Developed Grains in cm² = 4A	Mean Diams. Undeveloped Grains in cm $= \sqrt{\frac{A}{0.785}} = d$	Mean Diams. Developed Grains in cm $= 2\sqrt{\frac{A}{0.785}} = 2d$	Photometric Constant $P = 61 \times 2d$
3	0.19×10^{-8}	0.75×10^{-8}	0.5×10^{-4}	1.0×10^{-4}	0.0061
9	0.56×10^{-8}	2.25×10^{-8}	0.85×10^{-4}	1.7×10^{-4}	0.0104
18	1.13×10^{-8}	4.5×10^{-8}	1.2×10^{-4}	2.4×10^{-4}	0.0147
36	2.25×10^{-8}	9.0×10^{-8}	1.7×10^{-4}	3.4×10^{-4}	0.0207
Sum	4.13×10^{-8}	16.5×10^{-8}			

TABLE II

Exposures in Seconds

4A	0	4		16		64		256	
	No. Devel Grains	No. Developed Grains per cm^2 = N	Density $= 4\frac{NA}{2.3} = D$	N	D	N	D	N	D
0.75×10^{-8}	0	5.3×10^{-5}	0.0018	7.4×10^{-5}	0.0022	500×10^{-5}	0.160	850×10^{-5}	0.277
2.25×10^{-8}	0	87×10^{-5}	0.085	105×10^{-5}	0.103	286×10^{-5}	0.280	329×10^{-5}	0.322
4.5×10^{-8}	0	49×10^{-5}	0.096	75×10^{-5}	0.147	133×10^{-5}	0.260	139×10^{-5}	0.272
9.0×10^{-8}	0	18×10^{-5}	0.070	30×10^{-5}	0.117	36×10^{-5}	0.141	37×10^{-5}	0.145
16.5×10^{-8}	0	159.3×10^{-5}	0.253	217.4×10^{-5}	0.369	955×10^{-5}	0.841	1355×10^{-5}	1.016

Svedberg gives no data for the number of fogged grains so that these could not be taken into account in the tables. In Table II are shown (see also Fig. 6) the numbers of developed grains (exclusive of fogged grains as stated), for each exposure, together with densities to correspond (using 4A as the projective area for the developed grain), and also the additive or total densities. These total densities, it will be seen, by comparison with the total densities for the plate given in Svedberg's paper, as shown in Fig. 7 and Table III, are in the neighborhood of four times higher than those of the latter, whereas, if Higson's method of calculation is correct and if Svedberg's method is reliable, the values should agree.

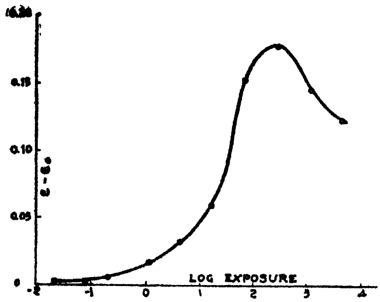

Fig. 7

TABLE III

Density (= Extinction Coefficient)

Time of Exposure in seconds	Total density	Density less fog
0	0.105 (= ϵ_0)	0
0.02	0.109	0.004
0.08	0.109	0.004
0.2	0.112	0.007
1	0.124	0.019
4	0.138	0.033
16	0.165	0.060
64	0.258	0.153
256	0.283	0.178
1024	0.250	0.145
4096	0.229	0.124

The most plausible explanation of this large discrepancy appears to be a fallacy in Higson's assumption that in general the developed silver grain has twice the diameter of the original bromide grain (i. e., 4 times the area). It is known

for instance, that certain developers, such as phenylenediamine, and hydrazine give developed grains considerably smaller than the original grain. Of course, it may be argued that these developers are not capable of giving complete development or perhaps they cause part of the silver to be dissolved. However, that may be, there does not appear to be sufficient experimental evidence for Higson's assumption. Work on this point, namely the determination of the ratio of the size of developed to undeveloped grain for various developers is much to be desired, and is about to be investigated in this laboratory by Mr. A. P. H. Trivelli.

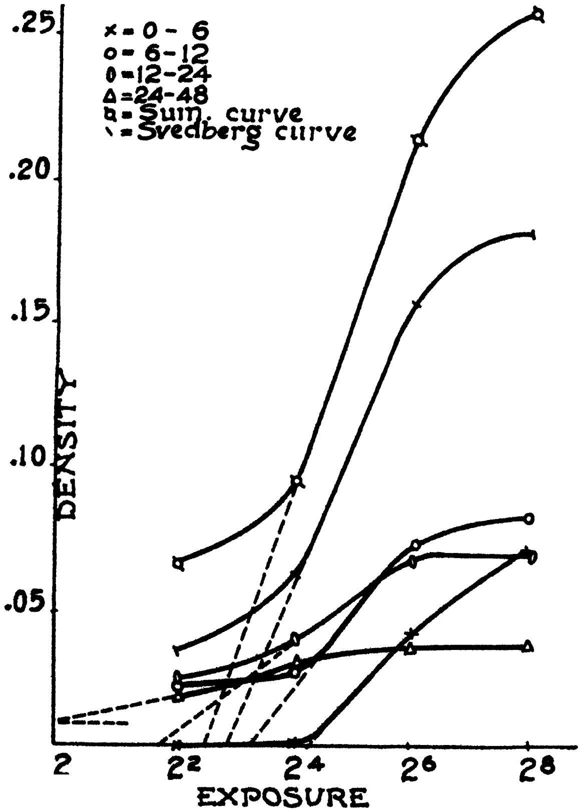

Fig. 8

TABLE IV

Exposure in Seconds

A	0	4		16		64		256	
	No. Devel. Grains	No. Developed Grains per $cm^2 = N$	Density $= \frac{NA}{2.3} = D$[1]	N	D	N	D	N	D
0.19×10^{-8}	0	5.3×10^{-5}	0.0005	7.4×10^{-5}	0.0006	500×10^{-5}	0.040	850×10^{-5}	0.069
0.56×10^{-8}	0	87×10^{-5}	0.0013	105×10^{-5}	0.026	286×10^{-5}	0.070	329×10^{-5}	0.081
1.13×10^{-8}	0	49×10^{-5}	0.024	75×10^{-5}	0.037	133×10^{-5}	0.065	139×10^{-5}	0.068
2.25×10^{-8}	0	18×10^{-5}	0.0175	30×10^{-5}	0.029	36×10^{-5}	0.035	37×10^{-5}	0.036
4.13×10^{-8}	0	159.3×10^{-5}	0.063	217.4×10^{-5}	0.092	955×10^{-5}	0.210	1355×10^{-5}	0.254

[1] D, in this table = 1/4 in Table II.

If we assume that the fully developed grains in Svedberg's work were of about the same size as the undeveloped grains (some previous observations by one of us on the size ratio of developed to undeveloped grains using a developer similar to that of Svedberg substantiate this assumption), then the density values calculated from Svedberg's data on this basis, give D-log E values very close to those of the latter, as shown by comparison of Fig. 8 and Table IV with Fig. 6 and Table III above.

Our calculations are based on the mean projective areas given by Svedberg. The maximum and minimum values of his four classes, particularly the larger sizes which are the most important, are quite wide apart so that the agreement just shown is all the more striking.

Svedberg's work on solarization and hydrogen peroxide action in this connection need not be discussed at present.

We reproduce here the size-frequency distribution curve (Fig. 9) plotted from Svedberg's data; this curve of course does not include fog grains.

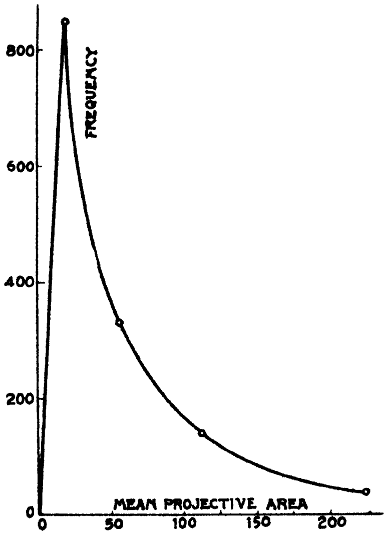

Fig. 9

Our work which was commenced before the papers of Slade and Higson, and of Svedberg, appeared, has as its object the investigation of the relation of grain, in the statistical sense, or of dispersity, to the sensitometric properties of emulsions. This requires methods of assay and determination of the size frequency curves. A discussion of the methods already developed in this direction by ourselves and others will be published shortly.

Rochester, N. Y.
November 12, 1920

ANHYDROUS YELLOW FERRIC OXIDE

BY JOHN H. YOE

Introduction

Ordinary ferric oxide is dark red in color, and when it is finely ground and diluted with finely ground, white materials, a series of mixtures is obtained of varying shades of pink. The indications are, however, that very fine particles of ferric oxide are yellow in color. Thus Keane[1] considered the yellow color of bricks to be due to finely divided ferric oxide whose agglomeration had been prevented by the presence of alumina and perhaps other substances. He also concluded that the so-called Mars pigments owe their yellow color to finely divided ferric oxide, stabilized by hydrous aluminum oxide. When these pigments are dehydrated they turn red, as the alumina is not present in sufficient quantity to prevent agglomeration of the ferric oxide. Keane also suggested that it should be possible to obtain a mixture of ferric and aluminum hydroxides which would remain yellow on heating.

Scheetz[2] carried out experiments to test this point. He prepared solutions of ferrous sulphate and aluminum sulphate in such proportions that after precipitation and oxidation they would give a product containing between 2 percent and 20 percent of ferric oxide. These solutions were treated with sodium carbonate, sodium hydroxide, and calcium hydroxide, respectively; the precipitates being washed, dried gradually, and finally heated to about 1000° C. With sodium carbonate and sodium hydroxide, non-uniform products of varying color were obtained. With calcium hydroxide, however, a series of products was obtained that varied in color from pale yellow (2 percent Fe_2O_3) to chocolate-brown (20 percent Fe_2O_3), all products containing less than eight percent of ferric oxide being uniformly yellow or buff. Since the mix-

[1] Jour. Phys. Chem., 20, 734 (1916).
[2] Ibid., 21, 570 (1917).

tures prepared in this way contained calcium sulphate in addition to the ferric and aluminum oxides, Scheetz was unable to show whether the stabilization of the yellow oxide was due entirely to the alumina, or whether the calcium sulphate played an important part.

The experiments described in the present article represent an extension of the work of Scheetz designed to indicate more definitely the nature of the stabilizing agent, and also an attempt to prepare anhydrous ferric oxide free from stabilizing agent.

Experimental

(1) Aqueous solutions of ferrous and aluminum salts were put in 2-liter, glass-stoppered bottles, and were precipitated with calcium, barium, or ammonium hydroxide, the reagent being added gradually, and the mixtures being shaken thoroughly after each addition. After complete precipitation the hydroxide mixtures were washed by decantation and filtered with the aid of suction. They were dried at 100° and finally heated to about 1000°, the temperature being increased gradually. The anhydrous products were ground in an agate mortar and were screened through a 150-mesh screen. In each case the product was lighter in color after grinding, the color growing lighter with decrease in the size of the particles. This is in accord with the work of Wöhler and Condrea,[1] and that of Weiser.[2] The results are summarized below. The color was always uniform unless otherwise indicated.

The experiments with calcium hydroxide upon solutions of ferrous and aluminum sulphates confirm Scheetz' results. The experiments with barium hydroxide show that similar mixtures containing barium sulphate instead of calcium sulphate likewise contain stable yellow ferric oxide.

The experiments with calcium hydroxide upon solutions of the chlorides show that the presence of calcium sulphate is not essential to the stabilization. It should, however, be

[1] Zeit. angew. Chem., 21, 481 (1908).
[2] Jour. Phys. Chem., 24, 277 (1920).

TABLE I

Oxides precipitated from Solution of the Sulphates, by

% Fe_2O_3	$Ca(OH)_2$	$Ba(OH)_2$	NH_4OH
1		Pale yellow (*a*)	
2	Yellow tinge		
3		Yellow (*b*)	
4	Cream		Yellow
6	Buff	Buff (*c*)	
8	Light brown		
10	Brown		Brown
15	Brown (darker)		
20	Reddish brown		Reddish brown

(*a*) Mixture contains 1 percent Fe_2O_3, 10 percent Al_2O_3, 89 percent $BaSO_4$.

(*b*) Mixture contains 3 percent Fe_2O_3, 10 percent Al_2O_3, 87 percent $BaSO_4$.

(*c*) Mixture contains 6 percent Fe_2O_3, 10 percent Al_2O_3, 84 percent $BaSO_4$.

TABLE II

Oxides precipitated from Solution of the Chlorides, by

% Fe_2O_3	$Ca(OH)_2$	$Ba(OH)_2$	NH_4OH
2	Pale yellow		Pale yellow
4		Dull brown	Yellow
6	Buff	Dull brown (darker)	Light brown
8			Light brown
10	Dull light brown		Brown
15			Reddish brown
20	Chocolate		Reddish brown (darker)

noted that in certain experiments not here recorded *pink* mixtures were obtained when calcium hydroxide was added to solutions of ferrous and aluminum chlorides, indicating that agglomeration is not invariably prevented.

The experiments with ammonium hydroxide upon solutions of both sulphates and chlorides show that yellow mixtures may be obtained in which ferric oxide and aluminum

oxide are the only components, thus showing that alumina may act as an effective stabilizing agent for finely divided yellow ferric oxide.

(2) In order to determine whether $CaSO_4$ or $BaSO_4$ could act as stabilizing agent, experiments were carried out in which solutions of ferrous sulphate, containing in some cases an excess of potassium sulphate, were precipitated by means of calcium or barium hydroxide. These experiments showed that when a quite large excess of $CaSO_4$ or $BaSO_4$ is precipitated with the ferric hydroxide, agglomeration of the ferric oxide may be prevented. For example, a product containing 6 percent Fe_2O_3 and 94 percent $BaSO_4$ was a uniform light buff, similar in color to the mixtures obtained in the presence of alumina. With smaller excesses of sulphate, however, reddish brown mixtures were usually obtained.

(3) Experiments were also conducted with the object of preparing a stabilized anhydrous ferric oxide, and then dissolving out the stabilizing agent. Thus a solution of ferrous and aluminum chlorides, in such proportions that after dehydrating the hydroxides the mixture would contain 8 percent Fe_2O_3 and 92 percent Al_2O_3, was precipitated by ammonium hydroxide. The precipitated hydroxides were dried in vacuum at 100° for ten hours. The apparently dry material was then removed from the flask, ground in an agate mortar, and covered with cold sodium hydroxide, different concentrations of sodium hydroxide being used in different experiments. The mixtures were allowed to stand at room temperature. At the end of twenty-four hours the aluminum hydroxide had been largely dissolved, but the residue had changed in color to a dark reddish brown, indicating that agglomeration of the ferric oxide had taken place.

Summary

Anhydrous yellow ferric oxide has been obtained in mixtures with (*a*) alumina, (*b*) calcium sulphate, (*c*) barium sulphate, (*d*) alumina and calcium sulphate, (*e*) alumina and

barium sulphate. The results confirm and extend the work of Scheetz.

Attempts to remove the stabilizing agent (e. g. by dissolving the alumina with NaOH) resulted invariably in an agglomeration of the ferric oxide, with a corresponding change of color from yellow to red.

University of Virginia
October, 1920

EXPERIMENTS ON WOOD CELLULOSE

BY WATSON G. HARDING

Parker[1] and Leighton[2] have shown that when absorbent cotton is heated at 100°–140° with dilute solutions of caustic potash or soda for a sufficient time and is then air-dried, the loss of weight is independent of the time of heating, provided this latter is not too short. Judged by this test, surgeon's cotton is about 92–93 percent pure, the balance consisting of about three percent moisture and 4–5 percent of material, presumably oxycellulose, which is carried into apparent solution by the alkali.

At the suggestion of Professor Bancroft similar experiments with wood cellulose were tried as part of the work for my senior thesis. Several sheets of wrapping paper were cut into strips and placed in a wide-mouthed, glass-stoppered bottle so that the moisture content would not vary materially. One-gram samples of the wrapping paper were weighed, placed in 500 cc round-bottomed flasks, covered with 100 cc of 1 percent NaOH, and boiled for the desired length of time with a reflux condenser. After boiling for about three hours the liquid becomes dark brown and consequently in many of the runs the caustic soda solution was changed halfway through the run, the spent liquor being drawn off and saved because it contained some suspended fiber. At the end of the run the flask was allowed to cool and the undissolved fiber was washed successively with dilute sulphuric acid (10 cc conc. acid per liter), dilute caustic soda (1 g per liter), water, alcohol, and ether. It was then transferred to a tared Gooch crucible, dried at a little over 100° and weighed. The amount of moisture in the original paper was found in three samples to be 5.24, 5.64, and 5.30 percent. The average of first and the last, 5.27 percent, was taken as the moisture content of the paper. The data as given refer to the paper as weighed. When filtering the solution, a dark brown pre-

[1] Jour. Phys. Chem., 17, 219 (1913).
[2] Ibid., 20, 32 (1916).

cipitate was observed which retarded the filtration a good deal. This was apparently dissolved by the dilute sulphuric acid used in washing the fiber. After this was noted, the filter was washed occasionally with dilute sulphuric acid to increase the rate of filtration. In some experiments the flasks were heated on the water-bath but it was found feasible to heat on a wire gauze over a free flame.

In Table I are given the effect of heating for times not to exceed twelve hours without changing the caustic soda.

TABLE I

Without water bath and without change of NaOH
1% NaOH and 102°

Hours	% Cellulose	Hours	% Cellulose
1	74.0	6	66.6
2	71.7	7	66.3
3	70.4	8	65.4
4	67.5	10	64.2
5	66.7	12	63.5

Even at the end of twelve hours no stationary state was reached. A longer series of experiments was made, changing the caustic soda halfway through the run. The data are given in Table II.

TABLE II

Without water bath and with change of NaOH
1% NaOH and 102°

Hours	% Cellulose	Hours	% Cellulose
5	67.0	15	62.8
6	65.9	20	61.3
7	65.3	25	60.8
8	64.3	30	60.3
10	63.7	33	60.0

The fiber is corroded a trifle more rapidly when the caustic soda is changed than when it is not—for all except the five-hour run. While no absolute equilibrium was reached, the rate of attack was very slow at the end. While still longer periods of heating should be tried, it looks as though the

particular paper used contained about 60 percent of material, which was not attacked by dilute caustic soda. It was hoped that this final product might be identical with cotton cellulose; but it gave a strong red color when a moist sample was treated with chlorine and then with a two percent solution of sodium sulphite, so heating with caustic soda has certainly not removed all the lignocellulose and may not have removed any of it.

Since heating for thirty hours is a trifle leisurely, a few experiments were made with more concentrated caustic soda and a shorter time of heating. The data are given in Table III.

TABLE III

Without water bath and with change of NaOH

Hours	NaOH	% Cellulose	Hours	NaOH	% Cellulose
5	2%	65.0	8	3	61.3
5	4%	63.7	8	4	59.1
6	3%	62.3	5.5	6	61.3

These data show that heating for 5.5 hours with a six percent caustic soda solution gives about the same result as heating for twenty hours with a one percent caustic soda. Of course there is no certainty that heating for twenty hours with six percent caustic soda might not decompose considerably more of the fiber. The time at my disposal did not permit of my making these determinations; but they should be made.

The preliminary results of these experiments are:

1. If wood cellulose is heated at about 100° with a dilute caustic soda for a sufficient length of time, the rate of attack becomes very low and may perhaps become zero.

2. With the sample of wrapping paper studied, heating with a one percent caustic soda solution for twenty-five hours or so left about sixty percent of the material undecomposed.

3. The caustic soda did not decompose all the lignocellulose and may not have decomposed any.

4. An approximately equal decomposition can be obtained by heating for about six hours with six percent caustic soda; but it is not yet known what would happen if the heating were prolonged.

Cornell University
June, 1917

THE NATURE OF SECONDARY VALENCE[1]

BY HOMER W. SMITH

PART II. PARTITION COEFFICIENTS

§ 1. Introduction

When an aqueous solution of any substance is shaken with an immiscible liquid some of the solute will pass from the water to the other liquid. The ratio of the concentration of the solute in the second liquid to the concentration in the water, after equilibrium has been attained, is called the distribution or partition coefficient. Under ideal conditions, the amount of solute passing into the second liquid would be proportionate to the concentration in the water, and the partition coefficient would be constant and independent of the total concentration; that is, we might write $C_2/C_1 = k$. This simple state of affairs is rarely met with, however, for practically all the substances with which we are concerned are dissociated in water, and many of them are associated in organic solvents. Since electrolytic ions do not exist in a non-dissociating solvent, such as xylene, and since associated molecules do not exist at great dilution in a dissociating solvent, such as water, both the dissociated and associated fractions of the solute in the two respective layers are removed from the system, so to speak, for neither can pass, as such, to the other layer. Hence, at a given total concentration, dissociation tends to lower the partition coefficient and association to raise it.

Any attempt to compare the partition coefficients of various substances would obviously be futile until both of these disturbing factors have been eliminated. Dissociation, which proceeds according to well known laws, can be corrected for on the assumption that the concentration in the second phase is proportionate to the undissociated fraction in the

[1] From the Department of Physiology, School of Hygiene and Public Health, Johns Hopkins University. The author is indebted to Mrs. R. A. Spaeth for generous assistance in the preparation and revision of the manuscript.

water. From the dissociation constant we can calculate the percentage dissociation at a dilution equivalent to the concentration in the water when equilibrium has been reached, and the partition coefficient then becomes: $C_2/C_1(1 - a) = k$. But there are only a few instances where this correction for dissociation suffices to hold the partition ratio constant over a large range of total concentrations, for most compounds, especially among the organic acids, are associated in organic solvents.

The mechanism involved in this association is comparable to that of dissociation, if we but think of the associated molecules in the organic solvent as similar to the undissociated molecules in water, and the single molecules in the organic solvent as similar to electrolytic ions. In concentrated solutions a larger fraction of the solute will be associated than in dilute solutions, and for intermediate concentrations all progressive degrees of decomposition of the associated fractions will be possible. But the analogy is imperfect, in that the maximum degree of association is unlimited; that is, the solute may be associated into aggregations of two, three, four, etc., molecules. Such aggregations as exist, however, would be expected to decompose at a rate constant and characteristic for each molecular species, comparable in a sense to the rate at which the single molecules decompose into electrolytic ions in water. This "decomposition constant" might be determined by studying both concentrated and dilute solutions, but there are reasons to believe that even this would not suffice to untangle the web. Water will dissolve in the second solvent, and thus upset the association constant, and the second solvent will dissolve in the water, and upset the dissociation constant. Furthermore, in some cases the partition coefficient increases with decreasing total concentration. This cannot be accounted for on the basis of either association in the second liquid, or dissociation in the water. It may be due to hydration. So complex do these disturbing factors become that it seems almost futile to attempt to correct for them on a stoichiometric basis. For our purposes it is necessary to have

values which represent the true tendency of the various species to pass from the water to the other solvent and any variations introduced by these disturbing factors would materially affect the interpretations to be based upon them. We have no way of knowing whether we have eliminated the disturbing factors or not, except as we anticipate in some measure the results which we may reasonably hope to obtain.

Before beginning a search for a suitable method of correction, several conditions were set down which any correction, to be satisfactory, would be expected to meet. If we compare the partition coefficients of a series of allied compounds, determined at the same total concentrations, into two solvents, such as chloroform and xylene, we see that the partition coefficients into the one solvent bear *approximately a constant ratio* to the partition coefficients into the other. This ratio is maintained fairly well so long as the compounds investigated have a similar dissociation constant; but when we include a compound which departs from the average in this respect, the ratio is materially altered. It seems a reasonable assumption that, if properly corrected for dissociation and association (if this latter occurs), this ratio would prove to be a constant. If we designate the *properly corrected* partition coefficient by $\mathfrak{P}$, we might then write

$$\frac{\mathfrak{P}_{\text{Chloroform}}}{\mathfrak{P}_{\text{Xylene}}} = \text{Constant.}$$

This simple relation should apply at least to nearly related substances, if we may judge from our experience with uncorrected partition coefficients. Furthermore, the ratio between the partition coefficients of any two compounds should be maintained regardless of the concentration at which the partition coefficients are determined, the nature of the solutes, and the nature of the second solvent. Since we are looking for certain relations among homologous compounds, we may in fairness anticipate them and require that our method of correction yield results which are subject to a reasonable interpretation. It would follow from the previous conditions that this interpretation would be essentially independent of the nature of the second solvent.

It would hardly be worth while to fill up several pages with test cases showing how methods of correction based upon dissociation constants and association factors fail in one or more respects to fulfill the above requirements. It is more to the point to discuss briefly the only method I have found so far which does appear to be satisfactory. It is unfortunately empirical and it cannot be said to be founded upon any physical-chemical experience whatsoever. The sole excuse for its use lies in the results obtained by it, and on these results alone can one base an opinion as to its validity.

We will consider the corrected partition coefficient, $\mathfrak{P}$, to be the ratio of the concentration in the second solvent to the concentration in the water (C_2/C_1) when the *concentration in the second solvent has some arbitrary and unitary value.* That is, $\mathfrak{P} = C_2/C_1$ when C_2 is 100 millimols, 10 millimols, 1 millimol, etc., per liter. This is similar to the method first advocated by Nernst; *i. e.*, deriving a constant ratio through the use of an exponential equation: $\frac{C_2}{C_1^y} = k$, where y is an uncharacterized exponent. The method differs from Nernst's in that no mathematical manipulation is involved, for in no case is y constant over a large range of total concentrations, and consequently the equation can never be ideally fulfilled. But we can determine the partition coefficient at suitable total concentrations so that we will actually pass, or approach very close to, a given concentration in the second solvent, and we thus reduce the possibility of introducing error through interpolation to a minimum.

A few cases have been cited from the literature to illustrate the application of this method of correction. If we compare the partition coefficients of several substances between water and several solvents, all of which solvents are relatively insoluble in water, we find that the ratio between the partition coefficients into one solvent and the partition coefficients into another solvent is a constant, and that it is independent of the concentration chosen for C_2.

The data upon which the following interpolations have been based are given in full in Section I of the tables given in

the experimental part of this paper. Below I have given only the concentration in the second solvent to which interpolation is made, the corrected partition coefficients, and the ratios between these partition coefficients.

TABLE I

	C_2 (m/L)	$\mathfrak{p}$ CCl_4	$\mathfrak{p}$ Toluene	$\mathfrak{p}$ Tol. / $\mathfrak{p}$ CCl_4	$\mathfrak{p}$ Benzene	$\mathfrak{p}$ Benzene / $\mathfrak{p}$ Toluene
Acetic acid	1000.0	0.10	0.12	1.20	—	—
Chloroacetic acid	1000.0	0.06	0.07	1.17	—	—
Phenol	1000.0	2.45	2.75?	1.12	4.3	1.56
Trimethylamine	1000.0	—	0.43	—	0.50	1.16
Pyridine	100.0	—	2.06	—	2.60	1.34
Chloroacetic acid	100.0	—	0.028	—	0.036	1.30
Butyric acid	1.0	0.115	0.16	1.39	0.215	1.26

It will be noticed that here we have a weak acid, a moderately strong acid, an alcohol, a weak base, and a ketone. Some of these we know to be associated in organic solvents; most of them we know are dissociated in water; nevertheless the ratios of the partition coefficients between water and carbon tetrachloride, and water and the other solvents are fairly constant. It is quite impossible to get this result with any other method of correction, especially with those compounds which show association in the organic liquids.

If, now, one of the solvents under comparison is soluble in water, the ratios vary with the different arbitrary values for C_2 which are chosen for extrapolation. Thus chloroform is much more soluble in water than is benzene or toluene. The ratio of the more soluble solvent over the less soluble one increases as lower values are chosen for C_2.

TABLE II

	C_2 (m/L)	$\mathfrak{p}$ $CHCl_3$	$\mathfrak{p}$ Benzene	$\mathfrak{p}$ $CHCl_3$ / $\mathfrak{p}$ Benzene	$\mathfrak{p}$ Toluene	$\mathfrak{p}$ $CHCl_3$ / $\mathfrak{p}$ Tol.
Acetic acid	1000.0	0.20	—	—	0.12	1.67
Phenol	1000.0	5.50	4.3	1.28	—	—
Chloroacetic acid	100.0	0.062	0.0365	1.70	0.028	2.22
Acetic acid	100.0	0.10	0.054	1.85	—	—
Butyric acid	1.0	0.385	0.215	1.79	0.16	2.40

If the two solvents are equally soluble in water, this divergence disappears, as can be seen from the comparison of chloroform and bromoform.

TABLE III

	C_2 (m/L)	$\mathfrak{P}$ $CHCl_3$	$\mathfrak{P}$ $CHBr_3$	$\frac{\mathfrak{P}\ CHCl_3}{\mathfrak{P}\ CHBr_3}$
Acetic acid	1000.0	0.20	0.148	1.35
Phenol	1000.0	5.50	4.30	1.28
Chloroacetic acid	1000.0	0.125	0.094	1.33
Ammonium	100.0	0.038	0.029	1.31
Picric acid	100.0	2.20	1.60	1.37

Though the evidence which has been given thus far is not very comprehensive, it is sufficient to show that so long as we use the same arbitrary value for C_2 for interpolation, the partition coefficients of various species so derived into any one solvent are subject to comparison; for since the partition coefficients of several compounds into two or more solvents bear a constant ratio to each other, all irregular influences arising in the nature of the second solvent are eliminated.

The values of the partition coefficient for any two compounds so obtained maintain a constant ratio to each other regardless of the nature of the second solvent, the total concentration, or the chemical nature of the solute. The truth of this last condition can be seen in Table IV.

TABLE IV

	C_2 (m/L)	$\mathfrak{P}$ Acetic acid	$\mathfrak{P}$ Chloro-acetic acid	$\frac{\mathfrak{P}\ \text{Acetic acid}}{\mathfrak{P}\ \text{Chloroacetic acid}}$
Chloroform	1000.0	0.20	0.125	1.60
Bromoform	1000.0	0.148	0.094	1.57
Toluene	1000.0	0.12	0.07	1.71
Carbon tetrachloride	1000.0	0.10	0.06	1.66
Chloroform	100.0	0.10	0.062	1.61
Benzene	100.0	0.054	0.0365	1.48
Chloroform	1.0	0.0725	0.0438	1.65
Xylene	1.0	0.030	0.0175	1.71

The partition coefficient is independent of the relative amounts of water and second solvent used.

TABLE V

Phenylacetic Acid into Xylene

	C_2	$\mathfrak{P}$
1 vol. xylene to 1 vol. water	$1m/L$	$0.510 \times 1 = 0.510$
1 vol. xylene to 2 vols. water	$0.5m/L$	$0.253 \times 2 = 0.506$
2 vols. xylene to 1 vol. water	$2m/L$	$1.02 \div 2 = 0.510$

We have now obtained fixed values for these partition coefficients where otherwise they would move indefinitely through a wide range because of at least five disturbing factors. The relative concentrations of any solute in the two solvents are indicative of the relative solubilities of the solute in those solvents. And since the concentration in the second solvent is always the same, the concentration in the water becomes a measure of the tendency of that solute to leave the aqueous environment and pass into the other environment, or a measure of the molecular fugacity. Further evidence will be brought out in the discussion to substantiate the method of correction, for by it are revealed many relations which have never been revealed by any other method of correction.

But it must be kept in mind that comparisons are valid only between values of $\mathfrak{P}$ *derived from the same arbitrary concentration in the second solvent* (C_2). For the purposes of this paper, the optional value of C_2 chosen for interpolation is 1.0 millimol per liter, for nearly all acids and bases are sufficiently soluble in water to permit our passing this concentration experimentally. A very short interpolation between values for C greater than 1 m/L and less than 1 m/L is all that is necessary to obtain the corrected partition coefficient $\mathfrak{P}$. In only a few cases (and the majority of these are cited from the literature) has this interpolation been made from values entirely above, or entirely below, this arbitrary concentration.

§2. Experimental

Aqueous solutions of known titer were shaken for three to five minutes with equal volumes of the second solvent. The mixture during shaking was contained in either a separatory funnel or a stoppered Erlenmeyer flask. Previous to shaking, the containing flasks and the solutions were brought to $25° \pm 0.5$, by immersion in a water bath, and after shaking the mixture was allowed to separate in the water bath. After separation, portions of the aqueous layer were titrated, and the concentration in the second solvent was determined by difference. The volatile nature of most of the materials studied and the extent of the work made it impractical to determine the concentrations in the second solvent directly. All titrations were made with standard hydrochloric acid and sodium hydroxide solutions, using phenolsulphonphthalein and methyl orange.

The bases were, for the most part, from freshly opened bottles of Kahlbaum's C. P. Reagents. For these, and for some of the acids, I am greatly indebted to Dr. Carl Voegtlin, whose co-operation in this matter has gone far to make this work possible. I am also indebted to Dr. E. K. Marshall, Jr., for some of the bases. The remaining preparations were secured from the Eastman Kodak Company. Inasmuch as this research was intended as a preliminary survey of the field, no attempt was made to obtain a degree of accuracy commensurate with physical research. None of the liquid chemical compounds was repurified, though practically all the crystalline compounds were recrystallized. The greatest difficulty in securing suitable checks lies in the extracting solvent. A slight contamination here of the proper sort will prove very disastrous. The xylene and chloroform were carefully repurified by shaking with strong alkali and then with 5 percent sulphuric acid, and by redistilling over a mixture of calcium oxide and calcium chloride. The other solvents were similarly repurified. The method offers little experimental difficulty, but a few sources of systematic error were found which may be worth mentioning. Solutions of both amines

and acids will decrease greatly in strength if violently shaken for a few moments, due evidently to increased surface adsorption. This adsorbed material diffuses very slowly into the solution again, and to guard against this effect, a sufficient interval of time should be allowed to elapse between sampling. The effect is especially pronounced immediately after making a solution of a liquid chemical compound, and after emulsification with an immiscible solvent. Five to ten minutes were always allowed after shaking to let the solution regain "diffuse" equilibrium. The amines, being very volatile, are easily lost from their aqueous solutions and the water layer should not be run out of a separatory funnel before titration. Samples can be taken direct from the funnel by blowing a small bubble of air through the pipette to expel the other solvent. Phenolsulphonphthalein gives a clean end-point with nearly all the amines (except the anilines of course), but it is not so satisfactory with the weaker acids. Where the partition coefficient is very small, an obscure end-point makes the determination very difficult. It is as satisfactory, however, as any other indicator for the purpose, and has the advantage that one can tell with it just what carbon dioxide is doing. By sucking through the pipette before sampling to clear out any carbon dioxide from the breath, difficulties from this source were eliminated.

In the following tables, the first section comprises material quoted from the literature, and the second section, the original contributions. The column headings need no explanation beyond the statement that unless otherwise indicated, all concentrations are expressed in *millimols per liter*.

SECTION I

	C_1	C_2	C_2/C_1	[illegible]	Reference[1]
BENZENE:					
Acetic acid, 25°	m/10 cc	m/10 cc			
	32.98	2.559	0.0776		
	25.867	1.580	0.061		
	13.821	0.554	0.040	1m/10 cc	
	5.793	0.159	0.027	0.054	H. and F.
Chloroacetic acid, 25°	m/10 cc	m/10 cc			
	71.856	3.177	0.0442		
	63.916	2.533	0.0396		
	21.191	0.729	0.0344	1m/10 cc	
	16.049	0.522	0.0325	0.0365	H. and F.
Phenol, 25°	m/cc	m/cc			
	0.3660	2.978	8.13		
	0.2578	1.254	4.87		
	0.1013	0.279	2.75	1m/cc	
	0.0272	0.062	2.29	4.3	R. and W.
Pyridine, 25°	m/0.05 cc	m/0.05 cc			
	0.000380	0.00110	2.9		
	0.000208	0.000546	2.62	1m/10 cc	
	0.000112	0.000274	2.50	2.6	H. and S.
Trimethylene, 25°	m/10 cc	m/10 cc			
	2.474	1.237	0.500		
	1.377	0.670	0.486	1m/10 cc	
	0.584	0.295	0.505	0.5	H. and F.

SECTION I (*Continued*)

	C_1	C_2	C_2/C_1	[illegible]	Reference[1]
BROMOFORM:					
Acetic acid, 25°	m/cc	m/cc			
	10.2	2.062	0.202		
	8.74	1.430	0.164	1m/cc	
	5.37	0.593	0.110	0.148	H. and L.
Ammonium, 25°	m/cc	m/cc			
	6.30	0.235	0.0373		
	4.18	0.131	0.0312	1m/10 cc	
	2.59	0.070	0.0271	0.029	H. and L.
Chloroacetic acid, 25°	m/cc	m/cc			
	9.69	1.20	0.124		
	9.61	0.813	0.084	1m/cc	
	8.85	0.649	0.073	0.094	H. and L.
Phenol, 25°	m/cc	m/cc			
	0.364	2.70	7.42		
	0.304	1.80	5.89	1m/cc	
	0.109	0.322	2.96	4.3	H. and L.
Picric acid, 25°	m/10 cc	m/10 cc			
	0.674	1.140	1.69		
	0.575	0.871	1.51	1m/10 cc	
CARBON TETRACHLORIDE:	0.475	0.655	1.38	1.6	H. and L.
Acetic acid, 25°	m/cc	m/cc			
	9.69	1.07	0.110		
	7.98	0.725	0.091	1m/cc	
	4.87	0.292	0.060	0.10	H. and L.

SECTION I (*Continued*)

	C_1	C_2	C_2/C_1	P	Reference[1]
Chloroacetic acid, 25°	m/cc	m/cc			
	11.3	0.551	0.0486		
	11.1	0.443	0.0398		
	10.7	0.362	0.0339		
	10.3	0.234	0.0229	1m/cc	
	9.6	0.159	0.0166	0.06	H. and L.
Phenol, 25°	m/cc	m/cc			
	0.489	1.47	3.01		
	0.213	0.141	0.665	1m/cc	
	0.140	0.072	0.514	2.45	H. and L.
CHLOROFORM:					
Acetic acid, 25°	m/cc	m/cc			
	2.056	0.349	0.169	1m/cc	
	1.527	0.207	0.136	0.20	
	1.188	0.135	0.114	1m/10 cc	
				0.10	R. and W.
20°	0.2696	0.01222	0.0453		
	0.1946	0.007586	0.0390		
	0.1269	0.00406	0.0320	1m/1000 cc	
	0.06445	0.00174	0.0270	0.025	D. and G.
Ammonium, 20°	gm/L	gm/L			
	7.861	0.2991	0.038		
	6.393	0.2439	0.038	1m/10 cc	
	5.160	0.1958	0.038	0.038	D. and C.

SECTION I (*Continued*)

	C_1	C_2	C_2/C_1	$\mathfrak{P}$	Reference[1]
Chloroacetic acid, 25°	m/cc	m/cc			
	7.70	0.840	0.109	1m/cc	
	7.23	0.707	0.0979	0.125	
	6.96	0.603	0.0866		
	3.65	0.253	0.0694	1m/10 cc	
	1.05	0.061	0.0590	0.062	H. and L.
Phenol, 25°	m/cc	m/cc			
	0.330	3.360	10.2		
	0.247	1.850	7.47	1m/cc	
	0.163	0.761	4.68	5.5	H. and L.
Picric acid, 25°	m/10 cc	m/10 cc			
	0.561	1.41	2.52		
	0.488	1.09	2.23	1m/10 cc	
	0.329	0.547	1.66	2.2	H. and L.
TOLUENE:					
Acetic acid, 25°	m/cc	m/cc			
	5.401	0.4477	0.0828		
	2.063	0.0864	0.0418		
	1.117	0.0343	0.0293	1m/1000 cc	
	0.334	0.0060	0.0181	0.010	H. and F.
25°	m/10 cc	m/10 cc			
	95.10	12.69	0.136	1m/cc	
	62.61	5.75	0.0919	0.12	H. and F.

SECTION I (*Continued*)

	C_1	C_2	$C_2 : C_1$	$\mathfrak{P}$	Reference[1]
Chloroacetic acid, 25°	m/10 cc	m/10 cc			
	92.04	5.434	0.059	1m/cc	
	80.68	3.358	0.0416	0.07	
	54.50	1.699	0.0312	1m/10 cc	
	33.46	0.926	0.0277	0.028	H. and F.
Phenol, 25°	m/10 cc	m/10 cc			
	4.75	14.96	3.15	1m/cc	
	2.20	4.66	2.12	2.75	H. and V.
Pyridine, 25°	m/cc	m/cc			
	0.0517	0.1129	2.18		
	0.0132	0.0275	2.08		
	0.0033	0.0066	2.00	1m/10 cc	
	0.0007	0.0010	1.44	2.06	H. and V.
Trimethylamine, 25°	m/cc	m/cc			
	0.0819	0.0363	0.443		
	0.0408	0.0177	0.433	1m/10 cc	
	0.0206	0.0087	0.422	0.43	H. and V.

[1] H. and F. Herz und Fischer: Ber deutsch. chem Ges., **37,** 4746 (1904); **38,** 1138 (1905). R and W. Rothmund und Wilsmore: Zeit phys Chem, **40,** 611 (1902). H and S Hantzsch und Sebaldt: Zeit phys Chem, **30,** 258 (1899). H. and L. Herz und Lewy. Zeit Elektrochem., **1905,** 818, Sitzungsber Schl Ges vaterländische Kultur; Naturwissenschäftl. Sektion, **1906,** 1. D and C. Dawson and McCrae Jour. Chem Soc, **79,** 493 (1901). H and V. Hantzsch und Vogt: Zeit. phys. Chem, **38,** 705 (1901). See also W. Herz Sammlung chemischer und Chemisch-technischer Vorträge, **15,** 1 (1910–11).

SECTION I (*Continued*)

	C_1 *m* cc	C_1/C_2	Average value $C_1/C_2(1-a)$	p (C_2 1*m*/1000 cc)	
ETHER:[2]					
Oxalic acid	0.1339	17.77	—		
	0.0887	21.66	—		
	0.0198	42.54	—		
	0.0103	61.38	—		
	0.0054	100.00	8.64	0.03	
Malonic acid	0.1478	10.94	—	—	
	0.1121	11 07	—	—	
	0.0862	11.28	—	—	
	0.0331	12.22	9.83	0.077	
Succinic acid	0.0217	7.81	—	—	
	0.0121	7.95	—	—	
	0.0059	8.39	—	—	
	0.0039	8.42	—	—	
	0.0023	8.79	7.45	0.123	
Glutaric acid	0.0280	3.72	—	—	
	0.0085	3.84	—	—	
	0.0072	3.91	—	—	
	0.0063	3.92	—	—	
	0.0056	3.93	3 58	0.253	

SECTION I (*Continued*)

	C_1 *m* cc	C_1 C_2	Average value C_1 $C_2(1-a)$	$\mathfrak{P}$ (C_2 1*m*, 1000 cc)
Pimelic acid	0.0098	0 7095	—	—
	0.00702	0.7170	—	—
	0.00480	0.7195	—	—
	0.00284	0.7480	—	—
	0.00179	0.7075	0 664	1 39
Suberic acid	0.00986	0.215	—	—
	0 00544	0.228	—	—
	0.00175	0 246	—	—
	0.00084	0.258	—	—
	0.00049	0.274	0.212	3.45
Azelaic acid	0 00064	0.0782	—	—
	0.00058	0.0800	—	—
	0.00051	0.0810	—	—
	0 00046	0.0823	—	—
	0 00033	0 0868	0.0637	9.5
Maleic acid	0.0253	13.27	—	—
	0.0196	14.40	—	—
	0.0143	16 06	—	—
	0 0100	17 78	—	—
	0 0054	23.70	6.71	0 0668

[2] Chandler: Jour Am Chem Soc, **30,** 696 (1908) Only a part of C.'s work is quoted in the above tables The figures given in the third column for C_1/C_2 $(1-a)$ are averages derived from a large number of concentrations. Note that in column 4 $\mathfrak{P}$ = C_2/C_1, not C_1/C_2 as given by C

Section II

The Partition Coefficients of the Acids between Water and Xylene, 25°

	C_1	C_2	C_2/C_1	**P**
Acetylsalicylic acid	17.30	7.25	0.419	—
	14.62	5.38	0.368	—
	7.15	2.00	0.280	—
	3.85	0.875	0.227	—
	3.28	0.719	0.219	0.222
iso-Amylacetic acid	0.85	7.95	9.37	—
	0.375	3.625	9.67	—
	0.212	2.170	10.25	—
	0.0792	0.8580	10.85	10.70
Anisic acid	0.682	1.50	2.20	—
	0.467	0.700	1.50	—
	0.381	0.494	1.30	—
	0.243	0.195	0.802	1.80
Benzilic acid	1.252	0.975	0.788	—
	1.029	0.643	0.625	—
	0.757	0.363	0.479	—
	0.448	0.133	0.300	0.800
Benzoic acid	4.19	17.4	4.15	—
	1.568	2.90	1.85	—
	0.842	0.865	1.03	—
	0.794	0.819	1.03	—
	0.737	0.678	0.92	1.10
Bromoacetic acid	37.40	1.15	0.0325	—
	26.70	0.90	0.0337	—
	23.30	0.70	0.0300	0.033
α-Bromopropionic acid	13.10	1.40	0.107	—
	10.50	1.00	0.095	—
	8.40	0.70	0.0835	—
	6.20	0.44	0.071	0.095
Bromosuccinic acid	61.70	1.85	0.03	—
	25.90	0.555	0.0214	0.0252
n-Butyric acid	8.20	1.30	0.159	—
	6.475	1.025	0.158	—
	4.500	0.700	0.156	0.158
sec.-Butyric acid	18.35	3.50	0.19	—
	9.575	1.625	0.17	—
	3.65	0.575	0.157	0.160

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	$\mathfrak{P}$
Camphoric acid	19.166	0.834	0.0436	—
	9.722	0.278	0.0286	—
	3.922	0.0776	0.0198	0.048
n-Caproic acid	2.80	17.7	6.32	—
	0.95	2.95	3.10	—
	0.75	2.15	2.86	—
	0.575	1.50	2.61	—
	0.3375	0.7375	2.18	—
	0.2625	0.5375	2.04	2.37
iso-Caproic acid	1.85	5.6	3.02	—
	1.325	3.375	2.54	—
	0.8125	1.6375	2.02	—
	0.4625	0.7500	1.62	1.75
o-Chlorobenzoic acid	4.55	7.45	1.63	—
	2.30	2.20	0.956	—
	1.75	1.325	0.757	—
	1.55	0.975	0.630	—
	1.19	0.600	0.505	0.635
Cinnamic acid	0.295	2.215	7.45	—
	0.225	1.025	4.55	—
	0.160	0.465	2.90	4.50
α-Crotonic acid	13.9	2.5	0.180	—
	6.3	0.80	0.127	—
	4.75	0.55	0.115	0.135
α-β-Dibromopropionic acid	7.35	1.45	0.197	—
	7.20	1.30	0.181	—
	5.20	0.75	0.144	—
	3.70	0.50	0.135	0.168
2,4-Dinitrobenzoic acid	10.95	1.10	0.100	—
	8.60	0.70	0.0815	—
	7.85	0.55	0.070	—
	6.78	0.40	0.059	0.10
3,5-Dinitrobenzoic acid	4.05	0.50	1.11	—
	3.15	2.95	0.936	—
	2.40	2.10	0.875	—
	1.53	1.11	0.720	0.70
Gentisinic acid	37.50	0.95	0.024	—
	30.50	0.61	0.020	—
	23.55	0.40	0.017	0.024

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	[illegible]
o-Iodobenzoic acid	1.10	2.20	2.00	—
	0.60	0.55	0.916	—
	0.325	0.175	0.538	1.15
β-Iodopropionic acid	13.75	4.46	0.325	—
	7.25	1.75	0.242	—
	6.60	1.44	0.218	—
	3.90	0.745	0.191	—
	2.97	0.525	0.1765	0.208
Hydrocinnamic acid	1.15	5.00	4.35	—
	0.85	3.40	4.00	—
	0.575	1.775	3.09	—
	0.375	0.975	2.60	2.75
Laevulinic acid	51.7	1.40	0.0271	—
	26.0	0.50	0.0192	—
	35.0	0.80	0.0228	0.0242
o-Nitrobenzoic acid	10.30	0.90	0.0874	—
	7.60	0.70	0.0920	—
	5.70	0.55	0.0965	—
	3.925	0.425	0.1080	0.085
m-Nitrobenzoic acid (1st recrystallization)	2.85	3.25	1.14	—
	2.30	2.30	1.00	—
	1.85	1.60	0.865	—
	1.325	0.95	0.718	0.73
m-Nitrobenzoic acid (2nd recrystallization)	3.00	3.35	1.11	—
	2.20	2.10	0.955	—
	1.60	1.375	0.860	—
	1.20	0.850	0.708	0.74
p-Nitrobenzoic acid	1.10	0.950	0.864	—
	0.962	0.7375	0.767	—
	0.725	0.4625	0.638	—
	0.681	0.4530	0.665	—
	0.3825	0.1750	0.458	0.90
Phenylacetic acid	5.00	5.00	1.00	—
	3.50	2.473	0.708	—
	2.60	1.5375	0.592	—
	1.60	0.7750	0.484	—
	1.26	0.5750	0.456	0.51

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	P
Phenylacetic acid (2 vols. xylene to 1 vol. of water)	3.575	4.825	1.35	—
	2.875	3.325	1.16	P[C_2 = $2m$ L]
	2.250	2.400	1.068	—
	1.400	1.275	0.910	1.02
Phenylacetic acid (2 vols. water to 1 vol. xylene)	4 90	3.05	0.623	—
	2.58	0 85	0.330	P[C_2=$0.5m$/L]
	1.75	0 35	0.200	—
	1.18	0.175	0.148	0.253
Phthalic acid	38.60	1 70	0.0430	—
	32.55	1.25	0.0384	—
	14.45	0.35	0.0243	0 0355
Piperonylic acid	0.865	1.14	1.32	—
	0 660	0.779	1.182	—
	0.3595	0 3142	0.875	1 29
Propionic acid	19 30	1.30	0.067	—
	9 20	0.60	0.065	—
	3 80	0.20	0.0528	0.066
Pyruvic acid	63.7	1.85	0.029	—
	45.8	1.10	0.024	—
	19.6	0 40	0.0204	0.0235
Resorcinilic acid	40.5	1.50	0.037	—
	26 8	0.80	0.0298	—
	19.2	0 50	0.0260	0.032
Salicylic acid	4.675	5.675	1.215	—
	3.075	3.075	1.000	—
	1.785	1.238	0.692	—
	1.350	0.862	0.638	—
	1.038	0.550	0.530	0.650
n-Valeric acid	8.40	11.6	1.38	—
	5.00	5.00	1.00	—
	2.30	1.70	0.74	—
	2.175	1.575	0.725	—
	1.500	0.925	0.616	—
	1.150	0.625	0.543	—
	0.6625	0.3125	0 472	0.635
iso-Valeric acid	6.15	3.15	0.512	—
	5.30	2.60	0.490	—
	4.275	1.925	0.450	—
	3.85	1.55	0.403	—
	2.35	0.875	0.372	—
	1.875	0.600	0.320	0.370

SECTION II (*Continued*)

The Partition Coefficients of the Bases between Water and Xylene, 25°

	C_1	C_2	C_2/C_1	$\mathfrak{P}$
Allylamine	6.50	1.30	0.200	—
	3.30	0.55	0.196	—
	1.85	0.35	0.189	0.198
n-Amylamine	5.08	14.92	2.94	—
	2.655	7.17	2.70	—
	1.875	4.275	2.28	—
	1.400	3.05	2.18	—
	1.335	2.67	2.00	—
	0.755	1.15	1.52	1.46
iso-Amylamine	2.65	5.10	1.92	—
	1.00	1.50	1.50	—
	0.80	1.175	1.47	—
	0.75	1.073	1.43	—
	0.55	0.700	1.28	—
	0.525	0.650	1.24	1.38
Anilin	0.378	2.00	5.3	—
	0.279	1.20	4.3	—
	0.203	0.67	3.3	—
	0.150	0.45	2.9	4.00
Benzylamine	6.32	13.68	2.16	—
	3.35	6.65	1.99	—
	1.58	2.42	1.53	—
	0.81	1.19	1.47	1.40
Benzylethylamine	1.40	18.60	13.4	—
	0.70	9.30	13.3	—
	0.35	4.65	13.3	—
	0.141	1.86	13.5	—
	0.103	1.368	13.6	13.4
Benzylmethylamine	1.138	8.86	7.80	—
	0.75	5.00	6.66	—
	0.226	1.20	5.30	—
	0.15	0.725	4.83	5.10
Bornylamine	0.08125	4.72	58.00	—
	0.0570	3.16	55.50	—
	0.0455	2.50	55.00	ca. 54.00
n-Butylamine	5.60	4.40	0.785	—
	2.40	1.50	0.665	—
	1.28	0.718	0.560	—
	0.671	0.328	0.490	0.60

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	P
iso-Butylamine	3.575	2.075	0.58	—
	1.775	0.975	0.55	—
	0.625	0.362	0.58	0.58
Camphylamine	0.0625	3.587	57.9	—
	0.0396	2.210	55.8	—
	0.0182	0.982	54.0	ca. 54.2
Coniine	0.935	9.065	9.7	—
	0.495	3.505	7.1	—
	0.265	1.735	6.5	—
	0.146	0.861	5.9	6.0
Diethylamine	12.68	7.42	0.59	—
	6.45	3 55	0.552	—
	4.075	1.925	0.472	—
	2.950	1.30	0.441	—
	2.72	1.28	0.470	—
	1.95	0.75	0.410	—
	1.45	0.55	0.380	0.44
Dimethylamine (in water)	17 78	2.22	0.125	—
	8.97	1.12	0.125	—
	3.55	0.430	0.121	—
	1.786	0 214	0.120	0.120
Dipropylamine	2.42	17.58	7.25	—
	1.45	8.55	5.90	—
	0.85	4.15	4.88	—
	0.575	2.325	4.04	—
	0.456	1.544	3.38	—
	0.425	1.525	3.59	—
	0.323	1.04	3.19	3.15
Ethylamine (in alcohol)	19.284	1.426	0.074	—
	9.255	0.745	0.0805	—
	3.654	0.346	0.0947	—
	1.7955	0.2045	0.1140	0.077
n-Hexylamine	2.80	17.2	6.15	—
	1.50	8.50	5.65	—
	0.7775	3.225	4.17	—
	0.625	2.325	3.88	—
	0.425	1.3375	3.14	—
	0.225	0.5875	2.61	3.05
n-Heptylamine	0.445	9.565	21.5	—
	0.438	9.562	21.8	—
	0.270	3.730	13.8	—
	0.152	1.848	12.3	—
	0.083	0.917	11.0	11.2

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	[illegible]
Methylamine (in water)	19.018	0.982	0.0517	—
	0.499	0.501	0.0528	—
	3.745	0.255	0.0680	—
	1.730	0.130	0.0750	0.051
Methylanilin	0.300	3.40	11.3	—
	0.185	2.10	10.9	—
	0.125	1.31	10.5	10.45
n-Methylpiperidine	7.33	12.67	1.725	—
	3.70	6.21	1.640	—
	2.40	3.40	1.420	—
	1.85	2.575	1.390	—
	1.70	2.300	1.350	—
	1.05	1.325	1.260	—
	0.683	0.934	1.365	—
	0.700	0.9375	1.340	1.20
Phenylethylamine	0.4125	1.51	3.64	—
	0.3437	1.13	3.29	—
	0.2380	0.763	3.20	—
	0.1940	0.582	3.00	3.20
Piperidine	7.00	4.00	0.57	—
	3.725	1.975	0.53	—
	2.850	1.300	0.456	—
	2.500	1.200	0.480	—
	1.850	0.750	0.406	—
	1.25	0.450	0.360	0.440
Propylamine	7.75	2.25	0.290	—
	4.80	1.30	0.270	—
	2.45	0.60	0.245	0.26
Pyridine	9.75	19.00	1.95	—
	4.80	9.50	1.98	—
	2.05	3.80	1.85	—
	1.00	1.90	1.90	1.95
Quinoline	0.470	9.40	20.0	—
	0.250	4.20	16.8	—
	0.116	1.80	15.5	14.0
Triethylamine	2.53	17.47	6.90	—
	1.49	8.51	5.72	—
	0.80	3.60	4.50	—
	0.75	3.25	4.33	—
	0.625	2.475	3.96	—
	0.3875	1.412	3.57	—
	0.3125	0.9875	3.16	3.17

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	p
Trimethylamine (in alcohol)	14.22	5.78	0.407	—
	6.97	3.03	0.435	—
	2.775	1.225	0.442	—
	2.13	1.00	0.47	0.47
Xylidene, 1, 3, 4	0.2875	3.3125	11.5	—
	0.1385	1.525	11.0	—
	0.1070	1.200	11.2	11.0
Xylidene, 1, 4, 3	0.2875	4.462	15.5	—
	0.1420	2.150	15.1	—
	0.0740	1.100	14.9	14.9
The Partition Coefficients of Acids between Water and Chloroform, 25°				
Acetic acid	20.9	2.00	0.0955	—
	13.8	1.00	0.0725	—
	8.35	0.45	0.0540	—
	5.85	0.235	0.0400	0.0725
Anisic acid	0.225	1.75	6.36	—
	0.206	1.206	5.85	—
	0.162	0.875	5.38	—
	0.125	0.625	5.00	5.50
Anthranilic acid	16.10	2.87	0.178	—
	10.00	1.54	0.154	—
	6.62	0.96	0.145	—
	4.50	0.60	0.133	0.148
Benzilic acid	0.640	1.75	2.74	—
	0.460	0.96	2.08	—
	0.2305	0.2885	1.25	2.12
Benzoic acid	1.137	4.55	3.96	—
	0.675	2.125	3.15	—
	0.599	1.84	3.07	—
	0.396	1.054	2 66	—
	0.3025	0.732	2.42	—
	0.2380	0.5625	2.36	2.65
Bromoacetic acid	32.00	2.08	0.065	—
	18.45	1.05	0.0570	—
	14.45	0.75	0.0519	—
	9.40	0.45	0.0478	0.0560
α-Bromopropionic acid	20.20	5.56	0.276	—
	13.00	3.48	0.268	—
	6.65	1.70	0.256	—
	4.40	1.10	0.250	0.248

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	[illegible]
n-Butyric acid	3.930	2.190	0.557	—
	2.290	1.252	0.546	—
	1.680	0.866	0.516	—
	1.402	0.710	0.506	—
	1.169	0.574	0.491	—
	1.040	0.488	0.470	0.530
sec.-Butyric acid	5.450	2.350	0.431	—
	3.190	1.275	0.400	—
	2.100	0.750	0.357	—
	1.025	0.350	0.342	0.385
Camphoric acid	19.25	10.35	0.538	—
	7.95	1.50	0.189	—
	4.30	0.525	0.116	0.120
n-Capronic acid	0.2125	1.4375	6.77	—
	0.1875	1.1375	6.08	—
	0.1158	0.6344	5.49	—
	0.0843	0.4281	5.07	6.1
iso-Capronic acid	0.4475	2.550	5.7	—
	0.2900	1.450	5.0	—
	0.2175	1.000	4.6	—
	0.1710	0.755	4.38	4.6
Chloroacetic acid	35.90	2.80	0.078	—
	28.60	1.55	0.0543	—
	16.10	0.50	0.0310	—
	12.00	0.30	0.0250	0.0438
o-Chlorobenzoic acid	1.075	2.690	2.50	—
	0.760	1.488	1.955	—
	0.649	1.072	1.655	—
	0.492	0.649	1.320	1.60
α-Crotonic acid	7.15	3.40	0.475	—
	5.10	2.125	0.417	—
	3.55	1.30	0.366	—
	2.35	0.75	0.319	0.340
α-*β*-Dibromopropionic acid	4.98	1.63	0.327	—
	3.54	0.985	0.278	—
	2.66	0.560	0.210	—
	1.85	0.313	0.169	0.280
2,4-Dinitrobenzoic acid	10.95	1.10	0.100	—
	8.60	0.70	0.0815	—
	7.85	0.55	0.070	—
	6.78	0.40	0.0590	0.10

SECTION II (*Continued*)

	C_1	C_2	$C_2 \; C_1$	$\mathfrak{p}$
3,5-Dinitrobenzoic acid	4.04	3.71	0.918	—
	2.855	2.38	0.834	—
	1.992	1.425	0.715	—
	1.450	0.975	0.672	0.68
Formic acid (average value)	32.2	1.00	0.031	0.031
Gentisinic acid	38.40	0.90	0.0234	—
	20.70	0.45	0.0217	—
	15.20	0.32	0.0210	0.0236
Glutaric acid	33.1	0.905	0.0273	—
	24.70	0.570	0.0231	—
	17.90	0.375	0.0210	0.020
Hydrocinnamic acid	0.177	1.770	10.00	—
	0.134	1.190	8.87	
	0.1058	0.835	7.90	—
	0.089	0.650	7.30	8.40
o-Iodobenzoic acid	0.473	1.990	4.21	—
	0.335	0.973	2.90	—
	0.287	0.680	2.37	—
	0.244	0.493	2.02	
	0.248	0.512	2.06	2.92
β-Iodopropionic acid	5.55	3.50	0.630	—
	3.70	2.12	0.572	—
	2.80	1.542	0.552	—
	1.61	0.805	0.500	—
	1.162	0.5375	0.462	0.515
Lactic acid	79.8	1.80	0.0226	
	50.4	1.00	0.0198	—
	32.8	0.60	0.0183	—
	26.9	0.43	0.0160	0.0198
Laevulinic acid	24.5	2.00	0.0817	—
	18.55	1.35	0.0728	—
	12.80	0.75	0.0586	0.063
o-Nitrobenzoic acid	8.65	3.35	0.388	—
	6.60	2.05	0.310	
	5.55	1.55	0.279	—
	2.775	0.45	0.162	0.225
m-Nitrobenzoic acid	0.950	1.625	1.71	—
	0.675	0.975	1.44	—
	0.4874	0.600	1.23	1.46

SECTION II (*Continued*)

	C_1	C_2	C_2/C_1	[illegible]
p-Nitrobenzoic acid	1.05	1.975	1.88	—
	0.75	1.175	1.57	—
	0.525	0.687	1.31	—
	0.364	0.400	1.10	1.50
Phenylacetic acid	0.715	1.542	2.16	—
	0.518	1.010	1.95	—
	0.425	0.785	1.845	—
	0.280	0.475	1.70	1.95
Piperonylic acid	0.250	1.0375	4.15	—
	0.2187	0.8125	3.71	—
	0.175	0.5812	3.32	4.00
Propionic acid	10.75	1.95	0.181	—
	7.12	1.175	0.165	—
	2.92	0.40	0.137	—
	5.65	0.85	0.153	0.163
Pyruvic acid	31.2	2.00	0.064	—
	16.90	1.00	0.0592	0.0592
Salicylic acid	2.625	6.575	2.50	—
	1.425	2.625	1.84	—
	1.138	1.862	1.64	—
	0.850	1.180	1.39	—
	0.608	0.730	1.20	—
	0.575	0.625	1.09	1.30
Succinic acid	48.00	0.95	0.0198	—
	34.90	0.60	0.0172	—
	20 50	0.30	0.0146	—
	13.50	0.15	0.0110	0.020
Valeric acid	1.825	4.625	2.53	—
	0.910	2.00	2.20	—
	0.650	1.35	2.08	—
	0.890	0.70	1.80	1.90
iso-Valeric acid	3.35	4.55	1.36	—
	2.45	2.90	1.182	—
	1.585	1.65	1.040	—
	1.239	1.162	0.94	0.91

The Partition Coefficients of the Bases between Water and Chloroform, 25°

n-Amylamine	0.2000	2.30	11.5	—
	0.1735	1.70	9.8	—
	0.150	1.20	8.0	—
	0.1168	0.6832	5.86	7.3

SECTION II (*Continued*)

	C_1	C_2	C_2 C_1	𝔓
Benzylamine	1.20	19.6	16.3	—
	0.65	9 55	14 7	—
	0.30	3.85	12 9	10 5
Diethylamine	4.350	17 95	4 13	—
	1.625	5 025	3.09	—
	0 800	2 000	2 50	—
	0 300	0.600	2 00	2 20
Dimethylamine (in water)	5 85	3 40	0 582	—
	4 55	2 65	0.582	—
	3.40	2 00	0.588	—
	2 20	1 275	0 580	—
	1 35	0 80	0 592	0 588
Ethylamine	25 50	20.70	0 78	—
	18 45	9 45	0 512	—
	10 20	4 80	0 470	—
	4 30	1.80	0 418	—
	2.525	1.00	0 396	—
	1 50	0 55	0 366	0.396
Methylamine (in water)	27 4	4 5	0.164	—
	13 5	1 9	0 141	—
	6 15	1.225	0.199	(Average)
	2.625	0.475	0.181	0 171
Triethylamine	0.425	9 575	22.5	—
	0 194	3.806	19 7	—
	0.0516	0.800	15.5	—
	0 0375	0 490	13.0	16 0
Trimethylamine (in alcohol)	4.85	14.95	3 08	—
	1.05	2.90	2.62	—
	0.60	1 50	2 50	—
	0.30	0.70	2.33	2 38
Piperidine	1.725	6 225	3.61	—
	1.200	3.625	3.02	—
	0.643	1.556	2.42	—
	0.400	0.800	2.00	2.15
Pyridine	1.45	16.25	11.2	—
	0.55	5.10	9 3	—
	0.30	2.2	7.3	—
	0.225	1.225	5.4	5 1

§ 3. Discussion

In the first part of this paper the generalized concepts of molecular volume and secondary valence were discussed in some detail. On the assumption that molecular volume is one of the essential or determining factors in all intermolecular relations of liquids we are going to use it in the analysis of the relations involved in partition coefficients.

The choice between molecular volume and molecular weight is not one which can be settled by literal proof. In the end it is a matter of interpretation and a decision must rest upon the relative value of the results to be obtained by the use of each. The reader is urged to keep in mind that such disclosures as are made through the use of molecular volume would not appear were one considering molecular weight; in fact, there would be no intelligible relationship whatever. This is especially true when we consider compounds containing halogens, ring formations, hydroxyl groups, ethylene linkages, etc., because then the relative differences in mass and volume become very great. It is a part of the purpose of this paper to establish the rôle of molecular volume in the intermolecular relations under consideration; and it is held that this rôle is established by the fact we are rewarded for its use with a significant simplification in these relations.

* * * * * * *

When we plot the logarithms of the partition coefficients of the amines and the acids into xylene against their respective molecular volumes we obtain the pictures reproduced in Figures I and II. Three outstanding facts are revealed by a glance at these pictures:

1. The observed points fall into several *series*, each of which is a straight line.

2. These *series* are all parallel.

3. The distances which separate the various *series* are related in a definite and periodic manner.

The equation for the straight line can be applied to any one of these *series* by extrapolating to $V_m = O$; with the constant of integration a thus obtained, the angular constant,

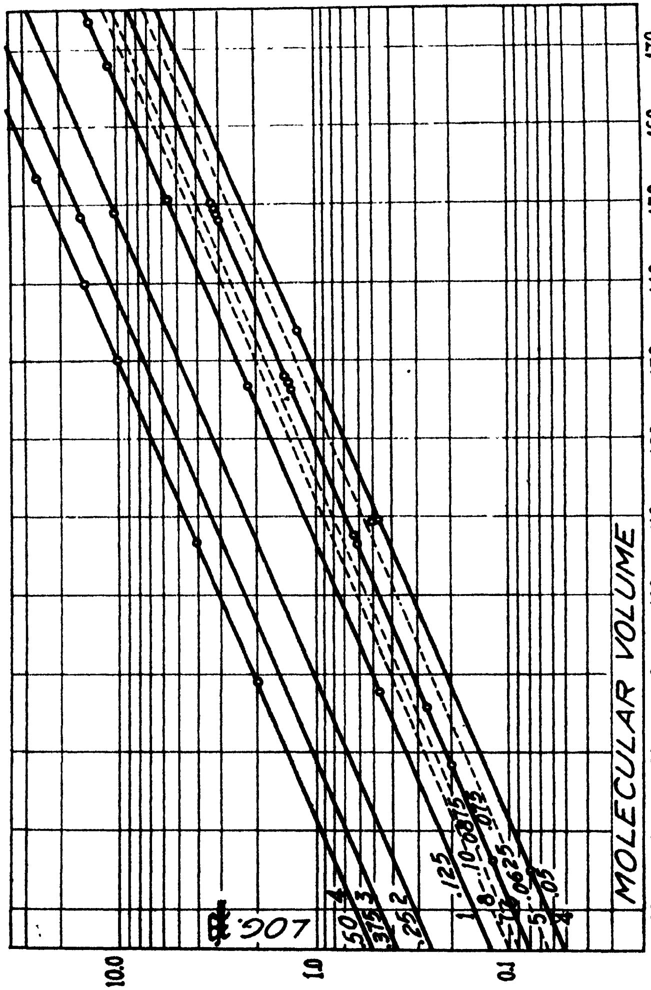

Fig. I
The Partition Coefficient of the Bases; Xylene

or constant of proportion, k can be calculated from the following equation:

$$\text{Log } 100\, p = \frac{V_m}{k} \pm a \ldots\ldots\ldots\ldots\ldots\ldots (1).$$

On the basis of careful extrapolations the angular constant k has been given the value 60.00. This constant is common to all *series* since they are parallel.

The compounds which have been studied will be considered according to the *series* in which they fall. In the

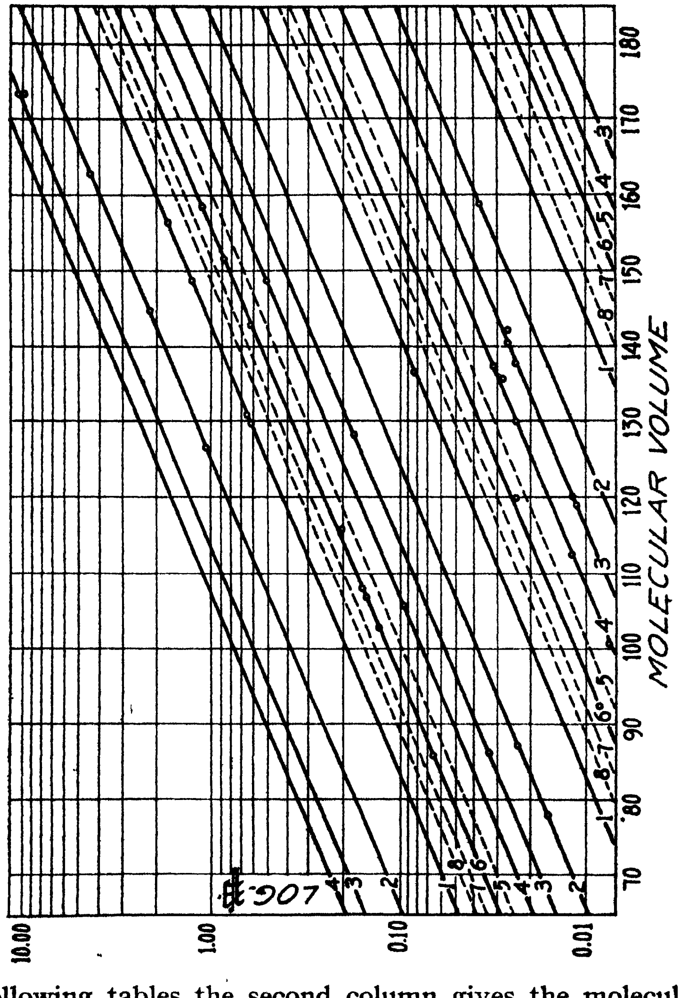

Fig. II
The Partition Coefficients of the Acids; Xylene

following tables the second column gives the molecular volumes; the italicized figures are observed values cited from Le Bas, and the others are calculated by Le Bas' rules. In column three, the osberved values of the partition coefficients $\mathfrak{P}$, are given and in the fourth column the values of $\mathfrak{P}$ as calculated from the equation given above using the *series* constant *a*. The ratios of the observed and calculated values in the fifth column are mathematical equivalents of statement 1 and 2 above.

TABLE I—THE AMINES

The Partition Coefficients of the Bases, by Series; Xylene

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc.}$	$\frac{\mathfrak{P}_{calc}}{\mathfrak{P}_{obs}}$
SERIES 4; a = +0.8239:				
Pyridine	*89.5*	1.95	2.07	106.1
Anilin	*106.6*	4.00	3.98	99.5
Methylanilin	129.6	10.45	9.19	114.0
Quinoline	*140.0*	14.0	14.36	102.4
Camphylamine	174.0	54.2	52.9	97.7
Bornylamine	174.0	54.0	52.9	97.9
SERIES 3; a = +0.6989:				
Xylidene, 1.4.3	*148.6*	14.9	14.98	100.4
SERIES 2; a = +0.5229:				
Xylidene, 1.3.4	*148.6*	11.0	10.00	90.8
SERIES 1; a = +0.2218:				
Trimethylamine	*88.0*	0.47	0.488	103.9
Benzylmethylamine	151.0	5.1	5.49	107.5
Heptylamine	169.5	11.2	11.14	99.6
Benzylethylamine	173.0	13.4	12.74	95.2
SERIES 8; a = +0.1249:				
SERIES 7; a = +0.06695:				
SERIES 6; a = ±0.0000:				
Methylamine	43.0	0.051	0.052	102.0
Dimethylamine	66.3	0.125	0.127	101.8
Allylamine	*78.5*	0.198	0.203	102.5

TABLE I (*Continued*)

	V_m	$\mathfrak{P}_{obs.}$	$\mathfrak{P}_{calc.}$	$\frac{\mathfrak{P}_{calc}}{\mathfrak{P}_{obs.}}$
Propylamine	*85.7*	0.26	0.268	103.0
iso-Butylamine	*106.3*	0.58	0.591	101.9
n-Butylamine	*106.8*	0.60	0.602	100.1
iso-Amylamine	*127.0*	1.38	1.310	95.0
Benzylamine	*127.4*	1.40	1.328	94.9
n-Amylamine	*127.5*	(1.46)	1.340	(91.7)
n-Hexylamine	*148.0*	3.05	2.925	96.0
Dipropylamine[1]	148.0?	3.15	(2.925)	(92.7)
	151.5		3.347	107.2
Triethylamine[1]	148.0?	3.17	(2.925)	(92.2)
	152.6		3.494	110.0
SERIES 5; a = —0.0792:				
SERIES 4; a = —0.1761:				
Ethylamine	*64.6*	0.077	0.0798	103.5
Piperidine	*108.8*	0.44	0.434	98.6
Diethylamine	*109.3*	0.44	0.442	100.2
Methylpiperidine	133.8	1.20	1.132	94.5
Coniine	*175.6*	6.0	5.63	94.0
			Av.,	100.8

[1] Both dipropylamine and triethylamine behave as though they had a volume nearly equivalent to hexylamine; secondary and tertiary nitrogen has a larger volume than primary nitrogen, and the low observed values may be due to impurities.

TABLE II —THE ACIDS
The Partition Coefficients of the Acids, by Series; Xylene

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc}$	$\frac{\mathfrak{P}_{obs}}{\mathfrak{P}_{calc.}}$
SERIES 4; a = +0.2354:				
SERIES 3; a = +0.1100:				
iso-Amylacetic acid	174.1	10.7	10 40	97.3
Heptoic acid	*174.6*	10.0	10 48	104.8
SERIES 2; a = —0.0655:				
Benzoic acid	*126.9*	1.10	1.12	101.8
Cinnamic acid	*162.7*	4.5	4.43	98.5
SERIES 1; a = —0.3666:				
Valeric acid	*130 0*	0.635	0.631	99.5
Salicylic acid	130.6	0.650	0.646	99.5
Piperonylic acid	148.7	1.29	1.29	100.0
Anisic acid	156.5	1.80	1.75	97.2
Hydrocinnamic acid	170.1	2.75	2 94	106 9
SERIES 8; a = —0.4634:				
SERIES 7; a = —0.5214:				
SERIES 6; a = —0.5884:				
Formic acid	41.5	(0.0125)[1]	0.0125	100.0
Acetic acid	*64.0*	(0.030)[1]	0.030	100.0
Propionic acid	*85.3*	0.066	0.068	103.0
α-Crotonic acid	102.1	0.135	0.130	96.3
sec.-Butyric acid	107.3	0 160	0 158	98.8
n-Butyric acid	*107.8*	0.158	0 161	102.0

TABLE II (*Continued*)

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc.}$	$\frac{\mathfrak{P}_{obs}}{\mathfrak{P}_{calc.}}$
β-Iodopropionic acid	115.0	0.208	0.213	102.5
iso-Valeric acid	129.5	0.370	0.371	100.2
o-Chlorobenzoic acid	143.3	0.635	0.631	99.4
p-Nitrobenzoic acid	152.5	0 900	0.898	99.8
o-Iodobenzoic acid	159.4	1.15	1.17	101.8
SERIES 5; a = —0.6676:				
m-Nitrobenzoic acid	151.9	0.73	0.731	100.1
SERIES 4; a = —0.7645:				
α-Bromopropionic acid	105.8	0.095	0.099	104.2
Phenylacetic acid	148.9	0.51	0.521	102.2
SERIES 3; a = —0.8894:				
Bromoacetic acid	84.5	0.033	0.0333	100.0
α-β-Dibromopropionicacid	127.8	0.168	0.174	103.5
SERIES 2; a = —1.0655:				
Acetic acid	*64.0*	(0.010)[2]	0.10	100.0
Chloroacetic acid	*78.0*	(0.0175)[1]	0.0172	98.3
Pyruvic acid	85.3	0.0235	0.0227	96.6
3,5-Dinitrobenzoic acid	175.8	0.70	0.732	104.5
SERIES 1; a = —1.3665:				
SERIES 8; a = —1.4634:				
SERIES 7; a = —1.5214:				

TABLE II (*Continued*)

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc}$	$\frac{\mathfrak{P}_{obs}}{\mathfrak{P}_{calc}}$
SERIES 6; $a = -1.5884$:				
Lactic acid	88.7	(0.00792)[3]	0.00774	97.7
o-Nitrobenzoic acid	150.8	0.085	0.0841	99.9
SERIES 5; $a = -1.6676$:				
SERIES 4; $a = -1.7645$:				
Oxalic acid	75.6	(0.003)[4]	0.0031	(103.3)
Malonic Acid	97.8	(0.0077)[4]	0.0073	(94.8)
Laevulinic acid	130.0	0.0242	0.0262	108.2
Itaconic acid	134.3	(0.0286)[4]	0.0298	(104.2)
Resorcinilic acid	136.4	0.032	0.0324	102.2
Acetylsalicylic acid	185.6	0.222	0.2132	96.0
SERIES 3; $a = -1.8894$:				
Succinic acid	120.0	(0.0123)[4]	0.0129	(104.8)
Gentisinic acid	136.5	0.0242	0.0243	100.3
Bromosuccinic acid	140.5	0.0252	0.0283	112.3
Glutaric acid	142.2	(0.0253)[4]	0.0302	(119.2)
2,4-Dinitrobenzoic acid	175.3	0.100	0.1077	107.7
Pimelic acid	186.6	(0.139)[4]	0.166	(119.2)
Suberic acid	208.8	(0.345)[4]	0.389	(112.8)
Azalleic acid	231.0	(0.95)[1]	0.913	(95.1)

TABLE II (*Continued*)

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc.}$	$\frac{\mathfrak{P}_{obs}}{\mathfrak{P}_{calc}}$
SERIES 2; a = —2.0655:				
Maleic acid	112.6	(0.00668)[4]	0.00647	(96.8)
o-Phthalic acid	155.6	0.0355	0.0337	95.0
Benzilic acid.	238.3	0 800	0.805	99.3
SERIES 1; a = —2.3665:				
SERIES 3, a = —2.8894:				
Camphoric acid	215.7	0.048	0.051	106.2
				Av., 101.4

NOTE: In many instances the partition coefficient between water and xylene is too low to be determined directly. It is possible to calculate this partition coefficient if the probable ratio between $\mathfrak{P}$ xylene and $\mathfrak{P}$ for another solvent is known. This calculation gives only one of several possible values for $\mathfrak{P}$ xylene, and therefore figures so obtained cannot be used in making comparisons of the constitutive behavior of several compounds But the fact that the values so obtained agree with the *Series* behavior is important, and so, in order to show this agreement and to complete the chemical groups in the above table, a few such calculated values have been included. For the derivation of the following ratios see §§4, 5, etc.

[1] Calculated from chloroform, ratio 2.5 to 1. §2, Sec. II.

[2] Calculated from toluene, ratio 1 to 1. Cf H and F, §2. Sec I. Also from chloroform, ratio 2 5 to 1. Cf. D. and G. (20°), §2, Sec. I.

[3] Calculated from chloroform, ratio 2 5 to 1.

[4] Calculated from ether, ratio 10 to 1. Cf Chandler, §2, Sec I

The Role of Molecular Volume

The above tables, through the application of Equation 1, establish the fact that all these *series* are straight lines and parallel.

The function of molecular volume may be briefly stated as follows:

In any series, the partition coefficient is a simple logarithmic function of the molecular volume.

That is, for any change in molecular volume, there is a corresponding change on a percentage basis in the partition coefficient. Since the angular constant is the same for both the amines and acids, the function of molecular volume is the same in both cases.

The Distance between Series

The most interesting aspect of these pictures is the distance which separates the various *series*. This distance is actually given by the respective values of a, as given in Tables I and II; but these values are logarithmic and their real significance is not evident until they are converted into their corresponding arithmetic values, or antilogs. Moreover, the values which have been given for a, and which are used in Equation I, are related to the particular ordinate: $V_m = O$, and would be numerically different were another volume chosen for comparison. So the universal relationship between the *series*, applying to any volume whatever, may be more easily understood if described in this manner:

The series delimit arithmetically related intervals or increases in the partition coefficient. These intervals fall naturally into octaves, each octave containing eight intervals. Each octave comprises an increase of 10 times in the value of the partition coefficient. In terms of $\mathfrak{P}$, *the first seven intervals are arithmetically equal; the eighth and last interval in any octave is arithmetically twice the value of each of the preceding seven.*

Since all experimental values fall upon one or the other of these *series*, the possible partition coefficients at any given volume are related to each other by definite multiples of a

common factor. $\mathfrak{P}_1$, which is given numerically in the value, in terms of $\mathfrak{P}_1$, of the first series of any *octave* at that volume.

Suppose we choose in Figure I the ordinate: $V_m = 54.2$; then on this ordinate the possible partition coefficients are as follows:

	Possible partition coefficients	Series number
First octave	1.25	1
	2.50	2
	3.75	3
	5.00	4
	6.25	5
	7.50	6
	8.75	7
	10.00	8
	12.50	10
Second octave	(25.00)	(20)
	(37.50)	(30)

(This arrangement has been illustrated at the left-hand margin of Figure I.)

The Octaves

Thus in passing up a particular ordinate from $\mathfrak{P} = 1$ to $\mathfrak{P} = 10$, we cross nine *series* or eight *intervals*. The value of the ninth *series*, instead of being nine times 1.0, is ten times 1.0, thus beginning another *octave*. This ninth series completes a group of eight *intervals*, seven of which are arithmetrically equal, each having a value of 1.0. The eighth *interval* has a value of 2.0 or twice the value of any *interval* in the preceding seven. A little consideration will show that this peculiar arrangement is nothing more than a consequence of dividing an increase of ten times in the value of $\mathfrak{P}$ into eight parts, when $\mathfrak{P}$ progresses logarithmically.

This may perhaps be better understood if we think of one *octave* as representing the total change which may take place in the molecule under given circumstances, and further suppose that the essential condition to be fulfilled is that an *octave* must end at ten times the value of $\mathfrak{P}$ at which it began.

The Series Numbers

From what has been said, it can be seen that, at any volume, the possible partition coefficients are related to each other as multiples of a common factor, and that the decimal value of the highest common factor depends simply upon the decimal value of $\mathfrak{P}$ under consideration. Now since the multiple number of any series, or its relative position in the *octave*, is always the same, the relative position of a particular *series* in any *octave* may be indicated by its multiple number; thus the *number* of any *series* refers to its position in the *octave*, but since all the *octaves* are identical in respect to the interrelations of the comprised *series*, any *series* may be considered irrespective of the particular *octave* in which it falls. In other words, *series 6* in one *octave* is comparable to *series 6* in any other *octave*.

The Importance of the Series Numbers

From the preceding paragraph it can be seen that each *series* possesses a characteristic individuality, so to speak, because of its position in the *octave*. That this characterization is of fundamental importance is borne out by a consideration of the constitutive relations disclosed in Table I and II.

Considering first Table I, we see that pyridine, aniline, methylaniline, quinoline, and collidin fall in *Series* 4; benzylmethylamine and benzylethylamine in *Series* 1; the majority of the aliphatic amines in *Series* 6, and the piperidine derivatives in *Series* 4. No general rules for constitutive behavior can be laid down, for there are obvious exceptions to the principle of chemically homologous groups, but despite the exceptions, one cannot but feel that chemical constitution is a very important factor in determining the *series* behavior.

Turning to Table II, we see that the aliphatic acids, up to and including iso-valeric, fall in *Series 6* (cf. aliphatic amines, also *Series* 6). Valeric acid slips from *Series* 6 to *Series* 1, and heptoic acid to *Series* 3. Caproic acid should presumably fall in *Series* 2.[1] The majority of the dibasic acids

[1] See footnote, p. 245.

fall in *Series* 3. These are only a few of the many instances which might be discussed in connection with constitutive behavior, but they are sufficient to show that:

The number of the series in which a compound falls is indicative of some fundamental property of that particular molecular species under the given conditions.

The Blank Series

If we summarize the distribution of compounds by *Series*, we see that the vast majority of them fall in *Series* 1, 2, 3, 4 and 6. (In the following table, the partition coefficients of the amines and acids between water and chloroform have been included. These partition coefficients will be considered in detail later on.)

Series number	No. of observed cases
1	19
2	17
3	23
4	22
5	(1)?
6	35
7	None
8	(1)?

This uneven distribution in the *octave* is emphasized by the behavior of chemically related compounds. Attention has already been called to the behavior of valeric acid, which left the company of formic, acetic, propionic, butyric and isovaleric acid in *Series* 6 to go into *Series* 1. It might have gone into *Series* 7 or 8, but it didn't. Again in the amines, benzylamine appears in *Series* 6, with the aliphatic amines, while benzylmethylamine and benzylethylamine avoid *Series* 7 and 8 to appear in *Series* 1. Trimethylamine and heptylamine also leave the other aliphatic amines in *Series* 6, to appear in *Series* 1. There are numerous other instances which might be mentioned to show that when a compound deviates from the behavior of allied compounds, it carefully avoids these blank *Series*.

The fact that there are so very few instances of compounds falling in *Series* 5, 7 or 8, suggests that the two which have been so far observed may be regarded somewhat as anomalies.[1] But since there is no apparent reason why compounds should not fall in these *Series* the time has not yet come to worry about them. The fact remains that *Series* 5, 7 and 8 appear to represent impossible or very improbable conditions, and this peculiar distribution in the *octave* may turn out to be significant in the final consideration of the underlying mechanism.

Some General Considerations

Secondary valence has already been defined as the force which binds molecules together. As a first step in the simplification of our problem, it was assumed that there is only one force involved in this union. It was pointed out that under this supposition, it was necessary to assume further that this force depended to a very great extent upon the chemical constitution of the molecule.

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[1] The exceptions to this distribution in *Series* 1, 2, 3, 4 and 6 are:

	Series No	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc}$
m-Nitrobenzoic acid (xylene)	5	0 73	0 73
n-Caproic acid (chloroform)	8	6 0	6 27
n-Caproic acid (xylene)	?	2 37	?
iso-Caporic acid (xylene)	?	1 75	?

m-Nitrobenzoic acid properly appears in *Series* 2 in chloroform and *iso*-caporic acid in *Series* 6; the former was repeatedly recrystallized and there can be no question of error in the partition coefficient for the sample investigated The caproic acids fall between *Series* 1 and 2 in xylene; it is interesting to note that their relative values are the same in both solvents:

$$\text{Xylene} \quad \frac{\text{Caproic acid} \quad 2.37}{iso\text{-Caproic acid} \quad 1\ 75} \quad 1\ 35$$

$$\text{Chloroform} \quad \frac{\text{Caproic acid} \quad 6\ 1}{iso\text{-Caproic acid} \quad 4.6} \quad 1.32$$

It was impossible to redistill either of the small samples of these compounds available, but it is hoped that new samples will correct this anomalous behavior.

The partition coefficient is an index of the relative solubility of a substance in the two solvents, and consequently it is an index of the extent of the forces involved in the process of solution. We have just seen that the partition coefficient depends upon two factors: one is molecular volume; the second factor, made evident in the rhythmic variation in the partition coefficient, can only be construed to indicate abrupt changes in the intensity of secondary valence characterizing the various molecular species. Since the rôle of molecular volume is identical in all cases, it is obligatory to assume that those compounds falling in a particular *series* have a common *intrinsic* intensity of secondary valence. This deduction is supported by the constitutive relations previously discussed; for if chemical constitution has anything to do with the intensity of secondary valence, we should certainly expect chemically homologous groups, such as the anilines, the aliphatic amines, the piperidines and the aliphatic acids to behave in a similar fashion.

If, then, compounds falling in the same *series* are alike in regard to secondary valence, the separation of the various *series* by definite distances must mean that.

The characteristic intensity of secondary valence in various molecular species differs by definite and related amounts.

In Part I, it was shown how the intensity of secondary valence associated with any molecular species depended upon the arrangement of the atoms in the molecule. These constitutive relations concern—and this is extremely important—only one or two atoms in the entire molecule. Yet these one or two atoms can endow the molecule with its characteristic secondary valence and thereby determine the molecular behavior. Such atoms (of which oxygen and nitrogen are the most important) may themselves vary in activity between wide extremes. Any variations relating to comparative molecular behavior must be attributed to changes in these particular atoms. (In the amines, it is obviously the nitrogen which is concerned; in the acids, it is principally the hydroxylic oxygen.) Now this rhythmic variation in secondary valence

is displayed by all types of compounds derived from amino nitrogen and acidic oxygen; the value of the unit increase is the same in every case, and the peculiar distribution in the *octave* (*i. e.*, in *Series* 1, 2, 3, 4 and 6) likewise relates to all the compounds so far studied. These facts lead us to an extremely important deduction, namely:

Secondary valence must be attributed to some part of the atom which is identical in its nature in, and common to, all atomic species.

The great susceptibility of secondary valence to constitutive relations and the fact that in some atoms it varies between wide extremes shows us that:

This atomic mechanism may vary in some atoms in its ability to make itself felt. It functions, so to speak, in a rhythmic fashion, and its activity is determined by the mode of chemical combination.

Since all atomic species may exist in the liquid state, *all atomic species must possess some secondary valence.* It is not possible to state any relation between this minimum, or basal, elementary value and the value which a given species will have when combined with other atoms in the molecule; so it may be necessary to consider ultimately both a basal elementary value and a basal atomic value in the state of chemical combination with other elements. In any event, it is probable that the fluctuations which we have been observing are in addition to this basal atomic value. Now the question arises, what are the limits to the fluctuations in secondary valence associated with any one atom? Examination of the available data shows that compounds containing only one atom characterized by variable activity, such as oxygen and nitrogen, are always encompassed within one *octave*. It is only when two such atoms are present in the molecule, as in the hydroxy acids, the dicarboxylic acids, etc., that the compound is found in the second *octave*, or more than eight intervals removed from any compound containing but one variable atom. This fact, together with the repetitive and self-contained nature of the *octave* and its exact arithmetic

equivalence to an increase in the partition coefficient of ten times, leads to the supposition that *one atom may furnish, in addition to its basal atomic value, one octave, or eight units of secondary valence. Two atoms may furnish presumably as many as sixteen, though constitutive interactions usually reduce the net amount.*

It does not follow that any atom will vary in this manner; carbon and hydrogen appear to possess a constant and low value.

If all the molecules under consideration contained only one variable atom, these molecules would all fall within the limits of one *octave.* But many compounds have been included in this study which contain several such atoms; hence these compounds are found scattered through two and even three *octaves.* Each successive *octave* must be looked upon as complete, however, though possibly adjoining other *octaves* by virtue of the superimposition of the last *series* of one on the first *series* of the other.

The Relation between Secondary Valence and Atomic Volume

It has long been recognized that atomic volumes are variable, and that the mode of chemical combination is the cause of these variations. Since there is a close relationship between the valence of an element and its elementary atomic volume, it is not surprising that the mode of chemical combination should influence the atomic volume in the combined state. We know practically nothing about the mechanism which underlies the variations in primary valence unions—those complex relations which G. N. Lewis has brought together under the term "polarity"—and it is impossible at the present time to quantitate these "polar-volume" relations. These atomic volume relations appear, however, to be of great importance in connection with the nature of secondary valence. Students of molecular physics, from Kopp's time on, have sensed a relation between atomic volume and secondary valence. What we are now calling secondary valence

has been called by divers authors "unsaturation," "subsidiary" and "residual valences," etc. The view a particular author took of this atomic mystery depended to a great extent upon the type of phenomena in which he was particularly interested. But it has been a common opinion that the "activity" of "unsaturated atoms" increased with decreasing volume. This is nicely illustrated in the behavior of oxygen. If we compare the boiling points and the solubility in water of an ether, an alcohol, an acid, and an ester, we see the close parallel which exists between the molecular behavior and the volume of the hydroxylic oxygen [Va O′].

	V_m	Va O′	B. P.	Sol. in 100 pts water, 20°
$C_2H_5OC_2H_5$	106.4	11.0	35 0°	7.30
$CH_3COOC_2H_5$	106.1	9 0	77.0	8 36
C_4H_9OH	102.1	6.4	116.8	8 35
C_3H_7COOH	107.8	6.4	163.0	20.00

Or, if we wish to compare various atomic species, the alkali metals are a classical example. The atomic volume increases in the order $Li < Na < K < Rb < Cs$. The salts of lithium are the most hydroscopic and the salts of caesium the least, thus indicating that the atoms with the smaller atomic volumes have the greatest affinity for water. The ionic velocity varies in the same order, lithium being the slowest and rubidium and caesium the fastest. The work of Jones and his collaborators showed that lithium was the most hydrated in aqueous solution, and caesium the least. In view of the facts that a particular atomic species varies in secondary valence according to the mode of chemical combination and that there are simultaneous changes in atomic volume which appear to be closely related to these secondary valence changes, the following assumption, though tentative, may aid us in the further analysis of the mechanism underlying atomic state:

The secondary valence associated with a particular atom in the combined state varies inversely as the volume of the atom;

the atomic volume, as well as the secondary valence, depends upon the mode of chemical combination.

§4. The Partition Coefficients into Chloroform

The partition coefficients of the acids and amines into chloroform have been analyzed in the same manner as were those into xylene. A comparison of Figure III with Figures I and II will show that the gross relations are identical. The angular constant, k, is the same in all cases, *i. e.*, 60.00, and hence the chloroform *series* are parallel to the xylene *series*. The inter-relations of *series* are the same so far as general proportionality is concerned, though the absolute values of a differ; in chloroform, P for a particular *series* at a given volume has just five times the value that it has in xylene.

In Tables III and IV the partition coefficients into chloroform have been tabulated just as were the partition coefficients into xylene. The calculated values given in these tables are derived through Equation I, using the *series* constants a as indicated, and the universal constant k = 60.00. The agreement between the observed and calculated values shows that the chloroform series constitute straight and parallel lines; since the *series* constants are based upon the ideal existence of *octaves* with related *series* as found in the case of xylene, it can readily be seen that there is no essential difference in the fundamental relationships in xylene and chloroform. The distribution of compounds by *series* has already been given in the previous section.

Partition Coefficient Ratios

One of the conditions imposed upon our method of correction was that the ratio $\frac{P_{\text{chloroform}}}{P_{\text{xylene}}}$ should be a constant. We can see now how this comes about. If we suppose that every compound falls in the same *series* in chloroform as it did in xylene, the ratio between the partition coefficients into the two solvents should always be 5.0, because, as has been said, a particular *series* in chloroform has a value of P at a given volume just five times its value at that same volume in xylene. But from Table V we see that this ratio is not always

TABLE III

The Partition Coefficients of the Bases, by Series; Chloroform

	V_m	$\mathfrak{P}_{obs.}$	$\mathfrak{P}_{calc}$	$\frac{\mathfrak{P}_{obs}}{\mathfrak{P}_{calc.}}$
SERIES 2; $a = +0.2219$:				
Pyridine	*89.5*	5.1	5.17	101.2
SERIES 1; $a = -0.1249$:				
Trimethylamine	*88.0*	2.38	2.197	92.3
Benzylamine	*127.4*	10.5	9.96	94.9
SERIES 8; $a = -0.2219$:				
SERIES 7; $a = -0.2799$:				
SERIES 6; $a = -0.3468$:				
Dimethylamine	66.3	0.588	0.573	97.5
n-Amylamine	*127.5*	(7.30)[1]	6.00	(82.2)
Triethylamine	*152.6*	16.00	15.72	98.5
SERIES 5; $a = -0.4260$:				
SERIES 4; $a = -0.5229$:				
Methylamine	43.0	0.171	0.173	101.0
Ethylamine	*64.6*	0.396	0.397	100.2
Diethylamine	*109.3*	2.20	2.21	100.4
Piperidine	*108.8*	2.15	2.17	100.8
SERIES 3; $a = -0.6478$:				
SERIES 2; $a = -0.8239$:				
				Av., 98.5

[1] Note that in Table V the perfect ratio 5 indicates identical behavior in both xylene and chloroform; consequently the extraordinarily high value may reasonably be attributed to impurities.

TABLE IV
The Partition Coefficients of the Acids, by Series; Chloroform

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc.}$	$\frac{\mathfrak{P}_{calc}}{\mathfrak{P}_{obs.}}$
SERIES 3; a = +0.8094:				
SERIES 2; a = +0.6335:				
SERIES 1; a = +0.3324:				
Benzoic acid	*126.9*	2.65	2.80	105.8
SERIES 8; a = +0.2355:				
Caproic acid	*152.5*	6.10	6.27	102.8
SERIES 7; a = +0.1775:				
SERIES 6; a = +0.1100:				
n-Valeric acid	*130.0*	1.90	1.89	99.5
Piperonylic acid	148.7	4 00	3.87	96.8
iso-Caproic acid	152.0	4.60	4.39	95.5
Anisic acid	156.5	5.50	5.23	95.2
Hydrocinnamic acid	170.1	8.40	8.81	105.0
SERIES 5; a = +0.0308:				
SERIES 4; a = —0.0655:				
n-Butyric acid	*107.8*	0.530	0.540	102.0
Salicylic acid	130.6	1.30	1.29	99.3
SERIES 3; a = —0.1904:				
Formic acid	41.5	0.031	0.0317	102.2
Acetic acid	*64.0*	(0.0725)	0.0752	103.7
Propionic acid	*85.3*	0.163	0.170	104.3

TABLE IV (*Continued*)

	V_m	$\mathfrak{P}_{obs.}$	$\mathfrak{P}_{calc}$	$\frac{\mathfrak{P}_{calc.}}{\mathfrak{P}_{obs.}}$
α-Crotonic acid	102.1	0.34	0.324	95.4
sec.-Butyric acid	107.3	0 385	0.396	102.9
β-Iodopropionic acid	115.0	0.515	0.532	103.2
iso-Valeric acid	129 5	0.91	0 928	102.0
o-Chlorobenzoic acid	143.3	1.60	1.577	98.6
Phenylacetic acid	148.9	1.95	1.955	100.2
o-Benzoic acid	159 4	2.92	2.926	100.2
SERIES 2; a = —0.3665:				
α-Bromopropionic acid	105.8	0.248	0.249	100.3
m-Nitrobenzoic acid	151 9	1.46	1.462	100.1
p-Nitrobenzoic acid	152.5	1.50	1.497	99.7
SERIES 1; a = —0.66756:				
Acetic acid	64 0	0 024	0.0251	104.6
Chloroacetic acid	78.0	0.0438	0.0429	97.9
Bromoacetic acid	84.5	0.0560	0.0550	98 2
Pyruvic acid	85.3	0.0592	0.0567	95 7
α-β-Dibromopropionic acid	127.8	0.280	0.290	103.6
SERIES 8; a = —0.7644:				
SERIES 7; a = —0.8224:				
SERIES 6; a = —0.8894:				
SERIES 5; a = —0.9686:				
SERIES 4; a = —1.0655:				
Anthranilic acid	135.0	0.148	0.153	03.3
3,5-Dinitrobenzoic acid	175.8	0 68	0.732	107.5

TABLE IV (*Continued*)

	V_m	$\mathfrak{P}_{obs}$	$\mathfrak{P}_{calc.}$	$\frac{\mathfrak{P}_{calc.}}{\mathfrak{P}_{obs.}}$
SERIES 3; a = —1.1904:				
Lactic acid	88.7	0.0198	0.0194	98.0
o-Nitrobenzoic acid	150.8	0.225	0.0210	93.4
SERIES 2; a = —1.3665:				
Laevulinic acid	130.0	0.063	0.0631	100.1
SERIES 1; a = —1.6675:				
Succinic acid	120.0	0.020	0.0215	107.7
Benzilic acid	238.3	2.12	2.01	94.8
SERIES 8; a = —1.7644:				
SERIES 7; a = —1.8224:				
SERIES 6; a = —1.8894:				
Gentisinic acid	136.5	0.0236	0.0243	103.0
Glutaric acid	142.2	0.029	0.0302	104.1
2,4-Dinitrobenzoic acid	175.3	0.100	0.1077	107.7
SERIES 5; a = —1.9686:				
SERIES 2; a = —2.3665:				
Camphoric acid	205.7	0.120	0.1153	96.3
				Av., 100.8
				Mean, 100.4

TABLE V

Partition Coefficients Ratios: $\frac{\text{Chloroform}}{\text{Xylene}}$

	$\mathfrak{p}_{\text{Xylene}}$	$\mathfrak{p}_{\text{Chloroform}}$	N_x	N_c	$\frac{\mathfrak{p}_{\text{Chloroform}}}{\mathfrak{p}_{\text{Xylene}}}$ or $5\frac{N_c}{N_x}$
Gentisinic acid	0.0242	0.0236	3	6	0.976
Bromoacetic acid	0.033	0.056	3	1	1.69
α-*β*-Dibromopropionic acid	0.168	0.280	3	1	1.66
p-Nitrobenzoic acid	0.90	1.50	6	2	1.66
Succinic acid	(0.0123)[1]	0.020	3	1	1.66
Salicylic acid	0.650	1.30	1	4	2.0
Acetic acid	(0.010)[2]	(0.025)[3]	2	1	2.50
Benzoic acid	1.10	2.65	2	1	2.41
sec.-Butyric acid	0.160	0.385	6	3	2.41
β-Bromopropionic acid	0.095	0.248	4	2	2.61
Camphoric acid	0.048	0.120	3	2	2.50
o-Chlorobenzoic acid	0.635	1.60	6	3	2.52
α-Crotonic acid	0.135	0.340	6	3	2.52
o-Iodobenzoic acid	1.15	2.92	6	3	2.54
β-Iodopropionic acid	0.208	0.515	6	3	2.48

[1] Calculated from ether, ratio 10 to 1; cf. §2, Sec I, Chandler.
[2] Calculated from toluene, ratio 1 to 1; cf. §2, Sec. I, H. and F.
[3] Cf. §2, Sec. I, chloroform, D. and G.

TABLE V (*Continued*)

	$\mathfrak{P}_{Xylene}$	$\mathfrak{P}_{Chloroform}$	N_x	N_c	$\frac{\mathfrak{P}_{Chloroform}}{\mathfrak{P}_{Xylene}}$ or $5\frac{N_c}{N_x}$
Laevulinic acid	0.0242	0.063	4	2	2.60
Propionic acid	0.066	0.163	6	3	2.47
Pyridine	1.95	5.1	4	2	2.62
Pyruvic acid	0.0235	0.0592	2	1	2.52
Anisic acid	1.80	5.50	1	6	3.06
Hydrocinnamic acid	2.75	8.40	1	6	3.05
Piperonylic acid	1.29	4.0	1	6	3.07
n-Valeric acid	0.635	1.9	1	6	2.99
n-Butyric acid	0.158	0.53	6	4	3.31
Methylamine	0.051	0.171	6	4	3.35
Phenylacetic acid	0.52	1.95	4	3	3.75
n-Amylamine	1.46	7.3	6	6	5.00
Diethylamine	0.44	2.2	4	4	5.00
Dimethylamine	0.12	0.588	6	6	4.90
Ethylamine	0.077	0.396	4	4	5.15
Piperidine	0.44	2.15	4	4	4.90
Triethylamine	3.17	16.00	6	6	5.07
Trimethylamine	0.47	2.38	1	1	5.06
Benzylamine	1.4	10.5	6	1	7.50

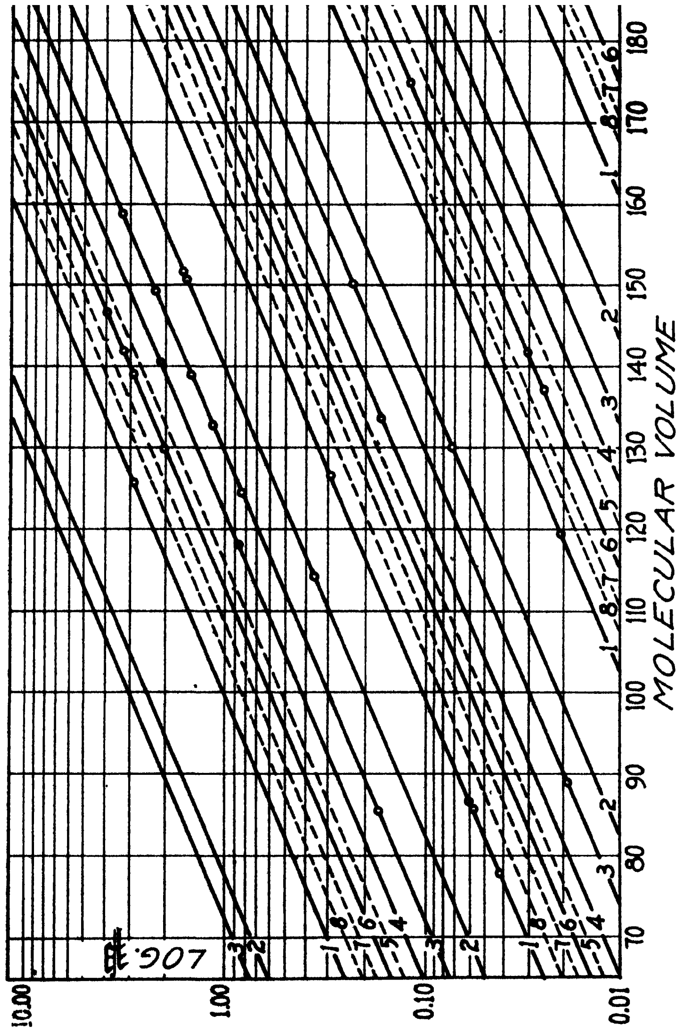

Fig. III

The Partition Coefficients of the Acids; Chloroform

5.0, but varies through a series of apparently related numbers running from 1.0 to 7.5. This is because compounds do not always fall in the same *series* in the two solvents. The possible ratios are limited, however, because the number of possible *series* is limited, and we may calculate the possible ratios on the basis that a compound may slip from any series in xylene

to any series in chloroform. It is only necessary to consider one *octave*, for as a matter of fact, compounds never slip out of one *octave*. If we let n_x represent the *series* number in xylene, and n_c the *series* number in chloroform, the possible ratios are given by the formula

$$5 \frac{n_c}{n_x} = r.$$

The 5 in the numerator is necessary because of the relative values of a particular *series* in the two solvents. The possible ratios have been tabulated below:

	n_x				
	1	2	3	4	6
n_c 1	5.0	2.5	1.66	1.25	0.833
2	10.0	5.0	3.33	2.50	1.66
3	15.0	7.5	5.00	3.75	2.50
4	20.0	10.0	6.66	5.00	3.33
6	30.0	15.0	10.0	7.50	5.00

Space does not permit a discussion of all the constitutive relations involved in these partition coefficients ratios, but a few of the more important points need to be emphasized.

It will be recalled that most of the aliphatic amines and the unsubstituted aliphatic acids fell in *Series* 6 in xylene. In chloroform we find the amines in *Series* 6 again, hence the ratio 5.0; the acids, however, occur in *Series* 3, reducing the ratio 2.5. It was further pointed out that the acids from valeric on, in the case of xylene, slipped up a *series* with each succeeding member. In chloroform we see that this slipping process is repeated, but it begins with one member earlier in the group, namely, with butyric acid. Thus formic, acetic and propionic acids come in *Series* 3, butyric acid in *Series* 4, valeric acid *Series* 6. (Notice how valeric acid again avoids the blank *Series* 5.)

Several reasons have already been given for believing that these *series* numbers indicate the relative intrinsic intensity

of secondary valence of the respective molecular species. This intensity, we have seen, depends upon the chemical constitution of the molecule and changes as a result of internal interactions between the component atoms. Now we see that this intensity is influenced not only by the chemical constitution of the molecule, but also by the environment. For though the same sample of butyric acid was used in determining the partition coefficient into xylene and chloroform, it does not behave in the same way towards the two solvents. In the former instance it fell in the same *series* as the preceding acids; in the latter instance, like valeric acid, it leaves the company of the preceding acids to pass into the next *series*. Numerous other instances of this same kind could be cited, all of which indicate some as yet obscure but definite principle underlying constitutive behavior. It is significant, however, that all these changes are in accordance with the *series* behavior, the *octave* distribution and some unformulated, yet obviously systematic relationship dependent upon chemical constitution.

But one important thing can be learned from these facts, and that is that *the intensity of secondary valence associated with a particular molecular species depends not only upon its chemical constitution, but also upon the nature of its environment.*

What constitutes Environment?

In both the systems which have thus far been considered, we have as components water and an immiscible liquid, with the solute distributed between them. It might be admitted that sufficient chloroform could dissolve in the water to cause these profound changes in the solute, but it is difficult to understand how xylene could exert any such influence in this manner for it is quite insoluble. But in both cases the second liquid is always intermolecularly connected, so to speak, with the water, through the interfaces and through the mutually contained solute. It must be through these channels, then, that equilibrium is established in such a system. The system consists of many molecular parts, each part capable of internal

changes, evoked by external influences; every part in delicate equilibrium with every other part.

Thus it is necessary to recognize an "equilibrium in state" for liquids; an equilibrium between the electrons in the atom and the forces acting between molecules. If this equilibrium is disturbed at any point through the introduction of a molecule of a dissimilar substance, a strain will be transmitted throughout the system, affecting in turn every part. In view of these facts it is preposterous to suppose that the sole force involved in the distribution of a solute between two regions of a liquid, or between two immiscible liquids, is "gaseous diffusion pressure." The processes of diffusion and osmotic pressure appear to be consequences of the law of free energy working itself out through this molecule to molecule mechanism, distributing the strain in some definite manner in compliance with the nature of the electrical forces involved. At equilibrium the system must possess a homogeneity of state, if we may call it that, for otherwise under the law of free energy relations the dissimilar molecules would be forced to the interfaces, and out of the system.

The facts which have been presented in this paper throw some light on the relations of the solute to its environment, and on the question of what constitutes this environment. The nature of these relations is held to be the most important fact, apart from the rôle of molecular volume itself, disclosed by a study of partition coefficients:

In any liquid system, all the parts of which are in cohesive contact, there exist equilibrated intermolecular forces involving all the contained molecules.

These forces have been shown to vary in a rhythmic manner, the observed variations being attributable both to internal (constitutive) and to external (environmental) influences.

Thus a condition of equilibrium or compensation exists between the electrical mechanisms within the molecule (or its contained atoms) and the electrical forces which constitute its environment.

This equilibrium is not effected through gross electromagnetic laws, but through some as yet unpostulated rhythmic mechanism involving (1) the valence electrons; (2) the atomic volume?; (3) the intensity of secondary valence.

Summary

1. An empirical method has been given for eliminating the disturbing influences of dissociation, association, etc., in the distribution of a substance between two immiscible liquids. The validity of this method is substantiated by the fact that it discloses certain relationships between the partition coefficients of various compounds which appear to accord with well known laws pertaining to solutions.

2. The partition coefficients of a large number of organic acids and bases have been determined between water and xylene and between water and chloroform.

3. The relations between these partition coefficients have been analyzed in terms of molecular volume. The out-standing facts disclosed by this analysis may be summarized as follows:

A. The observed points fall into several series, each of which is a straight line.

B. These series are all parallel.

C. The distances which separate the various series are related to each other in a definite and periodic way.

4. The following relations appear in the more detailed analysis of the facts summarized in 3.

A. In any series of compounds having the same intrinsic intensity of secondary valence, the partition coefficient is a simple logarithmic function of the molecular volume.

B. Secondary valence is rhythmic in nature. That is, it varies in different molecular species by related units. These differences in secondary valence are expressed in the partition coefficient by increases or decreases of definite amounts.

C. These unitary changes in secondary valence are related to each other by octaves, one octave comprising an increase of ten times in the numerical value of the partition coefficient at any given molecular volume.

D. Each octave contains nine hypothetical series (see 3, A), representing eight unit increases in the partition coefficient.

E. The first seven of these steps, or unit increases, are arithmetrically equal; the eighth is twice as large as any of the preceding seven. If we arbitrarily choose a volume at which the first series in the octave has a value in terms of $\mathfrak{P}$, of unity, then each of the first seven steps corresponds to an increase in the partition coefficient of an integral amount, or (1), 2, 3, 4 5, etc., the eighth step corresponds to an increase from 8 to 10; therefore the eight steps considered together (or one octave) corresponds to an increase from 1 to 10 or to an increase ten times in the value of $\mathfrak{P}$.

F. The relative position of a particular series in any octave may be indicated by its multiple number, or the number of times that the corresponding value of $\mathfrak{P}$, at a given volume, contains the highest common factor $\mathfrak{P}_1$ where $\mathfrak{P}_1$ represents the value of $\mathfrak{P}$ corresponding to the first series in the octave, at that volume. Thus the series numbers run from 1 to 8 inclusive.

G. Partition coefficients are observed in Series 1, 2, 3, 4 and 6; very rarely in 5, 7 or 8. (Evidence is considered in the text which indicates that Series 5, 7 and 8 probably represent unstable conditions.)

H. The differentiated nature of the octave, the peculiar distribution of compounds in the various series, and the principle of chemical homology which underlies this distribution by series all indicate that the series numbers have some very fundamental significance, in that they appear to represent some characteristic condition of the molecule as regards intensity of secondary valence.

5. Certain deductions of a more general nature have been based upon this analysis.

A. Since all the chemical compounds which have been studied so far behave in an identical manner so far as the foregoing points are concerned, it seems imperative to assume that secondary valence is to be attributed to some part of the atom

which is identical in its nature in, and common to all atomic species.

B. The variable and rhythmic nature of secondary valence shows that this atomic mechanism may vary in some atoms in its ability to make itself felt; that it functions in a rhythmic fashion and that its activity is determined by the mode of chemical combination.

C. A study of constitutive relations shows that the variations attributable to one atom are confined to one octave, or eight unit changes.

6. The series number, which has been shown to be a fundamental characteristic (see 4 H) depends not only on the chemical nature of the compound, but also on the nature of its environment. This fact, coupled with the fact that molecular volume is a determining factor in intermolecular relations, leads to a deduction of fundamental importance in the theory of solution, namely:

In any liquid system, all the parts of which are in cohesive contact, there exist equilibrated intermolecular forces involving all the contained molecules. A condition of compensation exists between these intermolecular forces and the electrical mechanism in the molecule and its contained atoms in which they have their origin.

Baltimore, Md.

NEW BOOKS

Alcoholic Fermentation. *By Arthur Harden. Second edition. 25 × 16 cm; pp. vii + 156. New York: Longmans, Green and Co., 1914. Price: $1.80.*— The titles of the chapters are: historical introduction; zymase and its properties; the function of phosphates in alcoholic fermentation; the co-enzyme of yeast-juice; action of some inhibiting and accelerating agents on the enzymes of yeast-juice; carboxylase; the by-products of alcoholic fermentation; the chemical changes involved in fermentation; the mechanism of fermentation.

In 1897 Eduard Buchner succeeded in preparing from yeast a liquor containing absolutely no cells, and yet capable of converting sugar into alcohol and carbon dioxide, p. 16. "In the light of this discovery the contribution to the truth made by each of the great protagonists in the prolonged discussion on the problem of alcoholic fermentation can be discerned with some degree of clearness. Liebig's main contention that fermentation was essentially a chemical act was correct, although his explanation of the nature of this act was inaccurate. Pasteur, in so far as he considered the act of fermentation as indissolubly connected with the life of the organism, was shown to be in error, but the function of the organism has only been restricted by a single stage, the active enzyme of alcoholic fermentation has so far only been observed as the product of the living cell. Nearest of all to the truth was Traube, who in 1858 enunciated the theorem, which was only proved for alcoholic fermentation in 1897, that all fermentations produced by living organisms are due to ferments secreted by the cells.

"Buchner's discovery of zymase has introduced a new experimental method by means of which the problem of alcoholic fermentation can be attacked, and the result has been that since 1897 a considerable amount of information has been gained with regard to the nature and conditions of action of the enzymes of the yeast cell. It has been found that the machinery of fermentation is much more complex than has been surmised. The enzyme, zymase, which is essential for fermentation, cannot of itself bring about the alcoholic fermentation of sugar, but is dependent on the presence of a second substance, termed, for want of a more reasonable name, the co-enzyme. The chemical nature and function of this mysterious coadjutor are still unknown, but as it withstands the temperature of boiling water and is dialysable, it is probably more simple in constitution than the enzyme. This, however, is not all; for the decomposition of sugar a phosphate is also indispensable. It appears that in yeast-juice, and therefore also most probably in the yeast cell, the phosphorus present takes an active part in fermentation and goes through a remarkable cycle of changes. The breakdown of sugar into alcohol and carbon dioxide is accompanied by the formation of a complex hexosephosphate, and the phosphate is split off from this compound and thus again rendered available for action by means of a special enzyme, termed hexosephosphatase. In addition to this complex of ferments, the cell also possesses special enzymes by which the zymase and the co-enzyme can be destroyed, and, further, at least one substance, known as an anti-enzyme, which directly checks this destructive action. It seems probable, mo eover,

that the decomposition of the sugar molecule takes place in stages, although much doubt yet exists as to the nature of these.

"At the present moment the subject remains one of the most interesting in the whole field of biolog'cal chemistry, the limited degree of insight which has already been gained into the marvellous complexity of the cell lending additional zest to the attempt to penetrate the darkness which shrouds the still hidden mysteries."

The conditions under which sugar can be fermented by yeast-juice are not very favorable to the attainment of extreme accuracy, p 31. "Yeast-juice contains glycogen and a diastatic enzyme which converts this into dextrins and finally into sugar. This process goes on throughout fermentation, tending to increase the sugar present and to make the apparent loss of sugar less than the sum of the products In spite of this it was found that a certain amount of sugar invariably disappeared without being accounted for as alcohol or carbon dioxide, and this whether the fermentation lasted sixty or a hundred and eight hours, and independently of the dilution of the juice This disappearing sugar amounted in some cases to 44 percent of the total loss of sugar, and on the average of twenty-five experiments was 38 percent Further information was sought by converting all the sugar-yielding constituents of the juice into sugar by hydrolysis before and after the fermentation. This process revealed the fact that when the glucose equivalent of the juice before and after fermentation was determined after hydrolysis with three times normal acid for three hours (and a correction made for the loss of reducing power experienced by glucose itself when submitted to this treatment), the difference was almost exactly equal to the alcohol and carbon dioxide produced. In other words, accompanying fermentation, a change proceeds by which sugar is converted into a less reducing substance, reconvertible into sugar by hydrolysis with acids
It has been shown by Buchner and Meisenheimer (1906) that glycerol is a constant product of alcoholic fermentation by yeast-juice, and no other source for this than the sugar has yet been found, so that it is not improbable that a small amount of sugar is converted into non-carbohydrate substances other than carbon dioxide and alcohol.

"It has also been shown that the deficit of sugar is not due to the formation of hexosephosphate, which has a lower reduction than glucose, and that the solution from which the sugar (either glucose or fructose) has disappeared actually contains some substance of relatively high dextrorotation and of low reducing power.

"However this may be, it may be considered as established that during alcoholic fermentation sugar is converted by an enzyme into some compound of less reducing power, which again yields sugar on hydrolysis with acids. The exact nature of this substance has not been ascertained, but it appears likely that the process is a synthetical one resulting in the formation of some polysaccharide, possibly intermediate between the hexoses and glycogen."

"The fermentation of glycogen by yeast-juice is of considerable interest, since it is known that the characteristic reserve carbohydrate of the yeast cell is glycogen, and moreover that in living yeast the intracellular fermentation of glycogen proceeds readily, whereas glycogen added to a solution in which yeast is suspended is not affected. Yeast-juice contains a diastatic enzyme

which hydrolyses glycogen to a reducing and fermentable sugar, so that in a juice poor in zymase to which glycogen has been added, the amount of sugar is found to increase, the hydrolysis of the glycogen proceeding more quickly than the fermentation of the resulting sugar, but the course of this enzymic hydrolysis of glycogen by yeast-juice has not yet been studied. As a rule, it is found both with juices from top and bottom yeast that the evolution of carbon dioxide from glycogen proceeds less rapidly and reaches a lower total than from an equivalent of glucose."

The general result of the experiments on the effect of antiseptics on the fermentation of sugars is to show, p. 37, "that quantities of antiseptics which are sufficient to inhibit the characteristic action of living cells have only a slight effect on the fermentative activity of yeast-juice. A large excess of the antiseptic in many cases produces a very decided diminution or total destruction of the fermenting power, and accompanying this a precipitation of the constituents of the juice. The decided increase of activity produced by small quantities of chloral hydrate, and to a less marked extent by chloroform and a few other substances, is of considerable interest. It is ascribed by Ducháček to a selective action on the proteoclastic enzyme, but without satisfactory evidence.

"Hydrocyanic acid, even in dilute solution, completely suspends the fermenting power of the juice, without, however, producing any permanent change in the fermenting complex, as is shown by the fact that when the hydrocyanic acid is removed by a current of air, the juice regains its fermenting power. In this respect hydrocyanic acid behaves precisely as with many other enzymes and with colloidal platinum. Sodium arsenite is a pronounced protoplasmic poison, which rapidly destroys the power of growth and reproduction in living cells, and was therefore applied to yeast-juice to differentiate between protoplasmic and enzymic action. It was, however, found that the action of this substance was complicated by some unknown factor and very irregular results were obtained. These phenomena appear to be of the same order as those produced by the addition of arsenates to yeast-juice, and will be discussed along with the latter."

It is possible that the home brewer does not realize the importance of adding phosphates, p. 42. "When a suitable quantity of a soluble phosphate is added to a fermenting mixture of glucose, fructose, or mannose with yeast-juice, the rate of fermentation rapidly rises, sometimes increasing as much as twenty-fold, continues at this high value for a certain period and then falls again to a value approximately equal to, but generally somewhat higher than, that which it originally had. Careful experiments have shown that during this period of enhanced fermentation the amounts of carbon dioxide and alcohol produced exceed those which would have been formed in the absence of added phosphate by a quantity exactly equivalent to the phosphate added in the ratio CO_2 or $C_2H_5OH : R'_2HPO_4$." The product formed is apparently a hexose-phosphate and the reaction may be written, p. 51:

$$2C_6H_{12}O_6 + 2R_2HPO_4 = 2CH_5OH + 2CO_2 + C_6H_{10}O_4(R_2PO_4)_2.$$

Experiments show that the fermentation of glucose and fructose by yeast-juice is dependent on the presence both of the enzyme and of another substance which is dialyzable and thermostable, p. 63. "This dialysable, thermostable

substance, without which alcoholic fermentation cannot proceed, has been provisionally termed the co-ferment or co-enzyme of alcoholic fermentation This expression was first introduced by Bertrand, to denote substances of this kind, and he applied it in two instances—to the calcium salt which he considered was necessary for the action of pectase on pecten substances, and to the manganese which he supposed to be essential for the activity of laccase. Without inquiring whether these substances are precisely comparable in function with that contained in yeast-juice, the term may be very well applied to signify the substance of unknown constitution without the coöperation of which the thermolabile enzyme of yeast-juice is unable to set up the process of alcoholic fermentation. The active agent of yeast-juice consisting of both enzyme and co-enzyme may be conveniently spoken of as the fermenting complex, and this term will occasionally be employed in the sequel.

"The co-enzyme is present alike in the filtrates from fresh yeast-juice and from boiled yeast-juice, and is also contained in the liquids obtained by boiling yeast with water and by washing zymin or dried yeast with water. Practically the only chemical property of the co-enzyme, other than that of rendering possible the process of alcoholic fermentation, which has so far been observed, is that it is capable of being decomposed, probably by hydrolysis by a variety of reagents, prominent among which is yeast-juice."

The extent to which the amino-acids of a medium, in which yeast is producing fermentation, are decomposed depends on the amount of available nitrogen and on the form in which it is present, p. 88 The subject is of great importance to the technologist because the great variety of the bouquets of wine and the aromas of brandy, cognac, arrack, rum, etc , may be referred very simply to the manifold variety of the proteins of the raw materials (grapes, corn, rice, sugar cane, etc.) from which they are derived.

The principal substances directly concerned in the process of alcoholic fermentation by yeast-juice appear, p. 119, to be the enzyme and co-enzyme of the juice, another enzyme called hexosephosphatase and, in addition, the sugar and phosphate together with the hexosephosphate formed from them. "During autofermentation two other factors are involved, the complex carbohydrates of the juice, including glycogen and dextrins, and the diastatic ferment by which these are converted into fermentable sugars. It is also possible that the supply of free phosphate is partially provided by the action of proteoclastic ferments on phosphoproteins. Under special circumstances the rate at which fermentation proceeds may be controlled by the available amount of any one of these numerous substances.

"When the juice from well-washed yeast is incubated, the phenomenon of autofermentation is observed. The juice contains an abundant supply of enzyme, co-enzyme, and phosphate or hexosephosphate, and in this case the controlling factor is usually the supply of sugar, which is conditioned by the concentration of the diastatic enzyme or of the complex carbohydrates as the case may be. When this is the case the measured rate of fermentation is the rate at which sugar is being produced in the juice, this being the slowest of the various reactions which are proceeding under these circumstances. If sugar be now added, an entirely different state of affairs is set up. As soon as any accumulated phosphate has been converted into hexosephosphate, the normal

rate of fermentation which is usually higher than that of autofermentation is attained, and, provided the excess of sugar be present, fermentation continues for a considerable period at a slowly diminishing rate and finally ceases. During the first part of this fermentation the rate is controlled entirely by the supply of free phosphate, and this depends mainly on the concentration of the hexosephosphatase and of the hexosephosphate, and only in a secondary degree on the decomposition of other phosphorus compounds by other enzymes and on the concentration of the sugar. The amount of hexosephosphate in yeast-juice is usually such that an increase in its concentration does not greatly affect the rate of fermentation, and hence the measured rate during this period represents the rate at which hexosephosphate is being decomposed, and this in its turn depends on the concentration of hexosephosphatase, which is therefore the controlling factor. As fermentation proceeds, the concentration of both enzyme and co-enzyme steadily diminishes, as already explained, probably owing to the action of other enzymes, so that at an advanced stage of the fermentation, the controlling factor may be the concentration of either of these, or the product of the two concentrations. The hexosephosphatase appears invariably to outlast the enzyme and co-enzyme. The condition at any moment could be determined experimentally if it were possible to add enzyme, co-enzyme and hexosephosphatase at will and so ascertain which of these produced an acceleration of the rate."

These selections give but an inadequate idea of the interesting nature of the book. *Wilder D. Bancroft*

The Principles of the Phase Theory. *By D. A. Clibbens 22 × 14 cm; pp. xx + 383. New York: Macmillan and Co., Ltd, 1920. Price: 25 shillings.*— In the introduction Professor F A. Freeth states that, with a few notable exceptions, singularly little attention has been paid to the subject of heterogeneous equilibrium in England. The various editions of Findlay's Phase Rule have either been overlooked or constitute notable exceptions. It is also stated that all the more complex one-component systems are now considered as at least pseudo-binary. Water may be theoretically pseudo-binary; but the changes take place so rapidly that it is experimentally a one-component system. In the preface the author says that the book does not give a systematic development of what he calls the Phase Theory because it is written primarily for the reader who is unfamiliar with the subject and he limits himself therefore to condensed systems formed from salts and their aqueous solutions; but excludes solid solutions. Instable equilibria are for the most part considered too difficult, though there is an erroneous reference to $Na_2SO_4.7H_2O$. On the very first page the author implies that the greater density of the atmosphere near the earth's surface is due to the weight of the upper layers resting upon them, which is not a helpful way of wording it. On the second page he says that, in practice we always work with masses which are sufficiently large to enable us to neglect the disturbing action of capillary forces, which is a rash statement. What he means to say is that he is only discussing systems in which the effect of capillary action is negligible; but he does not succeed in expressing himself accurately. On page 5 he says that in discussing solubility relations we can take the salt, hydrogen, and oxygen as components. That is likely to bother the student

because hydrogen and oxygen do not react appreciably in finite time at room temperature unless a catalytic agent is present. On page 12 it is stated that when two homogeneous and chemically indifferent solids are brought together they form two distinct phases as a rule. In the next line he says that the formation of solid solutions constitutes an exception; but we do not learn whether ice and salt are chemically indifferent solids above the eutectic point or whether the formation of a double salt is an exception to the rule It is another case of ill-chosen phraseology. On page 29 even this excuse will not suffice. The author says that if the surface of a salt solution is covered with a layer of an insoluble oil, the oil will prevent the evaporation of the water and we can consider the vapor phase as absent. Actually the partial pressure of the water vapor will not be affected by the pressence of the oil if we wait until equilibrium is reached. On page 58 the author resorts to italics in order to impress upon us that no solution can exist in true equilibrium with the heptahydrate of sodium sulphate. True equilibrium can occur. It is stable equilibrium which is impossible.

Besides the tendency to inaccurate statements, the author has the unfortunate gift of making an easy thing appear obscure. He has not even been thorough in his presentation because there is no reference to the occurrence of two liquid forms of the same substance in the melt, in spite of the fact that Olie has described a beautiful instance of this in the case of the hexahydrate of chromic chloride. It is difficult to see why this book was written or for whom it was written There is no justification for covering so little ground in three hundred and eighty pages The best thing that can be said for this book is that the author meant well *Wilder D. Bancroft*

Application of Dyestuffs. *By J Merritt Matthews. 23 × 15 cm; pp xii + 768. New York: John Wiley and Sons, Inc, 1920 Price, $10 00* — The author covers an immense amount of ground, the titles of the chapters being. introduction; chemical study of the fibers; scouring of the textile fibers, bleaching of wool and silk; bleaching of cotton; classification of dyes; application of acid dyes to wool; application of acid dyes to silk, cotton, etc.; representative acid dyes; stripping of colors and testing fastness of dyes; application of basic dyes; basic dyes on cotton; principal basic dyes; application of substantive dyes on cotton; substantive dyes on wool and silk; developed dyes on cotton and silk; application of mordant dyes; sulphur dyes, the vat dyes; aniline black, use of logwood in dyeing; minor natural dyes; the mineral dyestuffs; dyeing of fabrics containing mixed fibers; application of dyes to minor fibers such as linen, ramie, hemp, jute, and artificial silk; theory of dyeing; testing the fastness of colors; application of dyes to various materials; application of dyestuffs in the preparation of lakes, inks, etc.; testing of dyestuffs; miscellaneous tests in dyeing; chemical reactions of dyestuffs; analysis of textile fabrics; useful data for dyers and textile chemists.

There are a few slips Perkin did not discover mauve, p. 12, while working with Hofmann in Germany. There is apparently no justification for saying, p. 108, that sodium bisulphite in solution consists practically of sodium sulphite and sulphurous acid. It would be interesting to know why it is stated, p 247,

that in the dyebath the salts of the basic dyes are apparently dissociated into the dye bases and the acid.

The author is an expert in textiles and it is fair to assume that the technological part of his work is reasonably accurate. The reviewer does not care to question that. The theoretical part is hopelessly bad, however, and represents the view-point of about twenty years ago. The word adsorption does not occur in the index. There is nothing to show that none of the substantive dyes form true solutions. The action of charcoal in adsorbing dyes is mis-stated grotesquely, p. 583, and it would puzzle the author to give a satisfactory definition of a solid solution. The whole discussion is qualitative. Apparently the author has never heard of any quantitative measurements on dyeing; and consequently his attempts to account for the action of acids, bases, and assistants are depressing. It is quite possible that the author presents quite accurately the scientific views of the dye-users; but the dye-makers are a good deal further advanced than that. There is a great deal of valuable technical information in the book and the author should either have confined himself to a presentation of the part that he knew about or he should have made some attempt to study the scientific side. One would judge from this book that there had been no scientific advances since the days when Knecht wrote his book.

Wilder D. Bancroft

A Dictionary of Chemical Terms. *By James F. Couch. 18 × 13 cm; pp. iv + 204. New York: D. Van Nostrand Company, 1920. Price: $2 50.*—In the preface the author says: "This volume occupies a territory which is, at present, covered by no other book and is designed to serve the convenience of anyone who has occasion to read chemical literature The broad extension of chemical activities into apparently unrelated lines combined with specialization of interests has resulted in a complex and scattered terminology. It is often difficult and, in many cases, all but impossible, even with the best of literary facilities, to find a definition for many of the more recently introduced terms. Under such conditions it is not easy for the chemist to read intelligently chemical literature which is not rather closely related to his own narrow specialty.

"To assist in removing some of these difficulties this dictionary is offered to the chemical profession. It has been attempted to make it practical rather than academic and no pains have been spared to insure its accuracy and completeness. It has been subjected to detailed criticism and revision by a number of specialists in varied lines and the whole has been carefully edited.

"The treatment of the terms has been designed to lie somewhere between that of a standard English dictionary and that of an encyclopaedia; in most cases elementary terms have received more extended treatment than more advanced terms. Controversy has been avoided where possible; usually the commonly accepted definition has been given and, often, the conflicting views are stated. The author, however, does not wish to be understood as assuming the position of referee in any controversial matter treated, nor must the definitions be considered to represent his private opinion in all cases. The definition given is intended to represent the idea generally accepted by chemists at this time."

There seems to be a need for such a book and a hasty inspection indicates that the author has done his work well. As is to be expected there are some slips. The reviewer does not like the definition of boiling points, p. 26. A gel is not necessarily gelatinous, p. 89. It seems like straining a point to say that charcoal takes up gases because of the tendency to reduce the surface area, p 4. The cathode of a primary cell is not usually called the negative pole, p. 36. Most people will disagree with the statement, p. 29, that the force of adhesion is so minute as to be insensible and it is scarcely capillary pressure that makes a wetted wooden wedge split a rock. Few people will understand the paragraph on steam distillation, p. 65, and it is probable that the process seems mysterious to the author. There is some question whether false equilibrium is a synonym for metastable equilibrium, p. 77. The pressure-volume isotherms are less important in most cases than the various concentration isotherms and yet these latter are not mentioned, p. 111. The names, of Thomson, Wiedemann and van der Waals are mis-spelled. The reviewer looked in vain for such words as bar, Baumé, Brix, elutriation, foam, fog, and smoke. In some parts of England the eighth letter of the alphabet is not pronounced at the beginning of a word; but in this country the practice is to treat it as a consonant.

Wilder D. Bancroft

Notes on Chemical Research. *By W. P. Dreaper. Second edition. 18 × 12 cm; pp. xv + 195. Philadelphia: P. Blakiston's Son and Co, 1920 Price: $2.50*—The first edition was reviewed eight years ago (**17**, 562). It was only about one-third the size of this. There are new chapters on the nature of scientific knowledge and on observation and experiment. The book is now divided into two parts: scientific fact and method; practical research. Under practical research the headings of the chapters are: aims of practical science; practical investigation and the personal factor; laboratory research and works practice, works organization; efficiency and working conditions; large scale operations; the student and his course of training; the general recording of results and other matters.

On p. 175 the author states that the only sound method of instruction in research is "that original research carried on in a chemical department should be open to the personal inspection of all the students of the department at some stage of their training, and that they should have the opportunity of following this to the best of their ability Such a process brings the chemical department in line with the medical department (so far as practical research is concerned). It is submitted also that this should be one of the main branches of college training. As a secondary measure, the students, in groups, should repeat some classic (and easy) examples of research in all their detail. Just as training is imparted (in the general laboratory) in the methods of analysis, so instruction should follow (in the research laboratory) in the methods which make up and control research. This course seems so essential that it is again put forward as a definite aim."

This sounds well; but the reviewer is a trifle sceptical as to the way in which it would work out. Many people think that research is primarily a question of manipulative skill; but the essential thing is the point of view and the habit of mind, which can only be developed by practice. The author does not

believe this because he says, p. 180, that "in certain quarters it is held that students should enter upon a post-graduate course of research at the college. It is doubtful whether this course is a good one for the chemist except in cases where he confines his attention to laboratory work. In this case the further contact with research conditions, as these are carried out on academic lines, may prove useful in some cases, in others not," The reviewer is not quite sure what this paragraph means; but American practice is against the author's conclusions whatever they are. *Wilder D. Bancroft*

Eminent Chemists of Our Time. *By Benjamin Harrow. 20 × 14 cm; pp. xvi + 248. New York: D. Van Nostrand Company, 1920. Price: $2.50.*— In the preface the author says that he wished to write a history of our times by centering it around some of its leading figures "This book aims to fill the wants of three classes of men: 1. The chemist who wishes an account of the labors of some of the most illustrious men in his profession. 2. The scientist, other than the chemist, who desires information in a closely related field. What physicist can ignore the work of Mme. Curie? What biologist or medical man is not indebted to van't Hoff, Arrhenius and Fischer? And how has industry profited by the labors of Moissan and Perkin! These instances could be multiplied. 3 The layman who wants a non-technical account of some of the more remarkable achievements in a science which is entering more and more into our daily lives."

The book consists of chatty biographical sketches of Perkin, Mendeléeff, Ramsay, Richards, van't Hoff, Arrhenius, Moissan, Mme. Curie, Victor Meyer, Remsen, and Emil Fischer. Books of this sort are always worth while and this one is no exception to the rule. People like to read them and it is very desirable that students in chemistry should read them. The proof-reading is not as good as it might be, Lord Rayleigh's name, for instance, being mis-spelled nearly every time it occurs.

The reviewer was sorry to see the fallacy about atomic weights and copper ores cropping up again, p. 71. "As showing how quite unexpected practical applications may result from work of scientific interest only, the following may be cited: copper ore is purchased upon a metal value, established by chemical analysis, a value based upon the weight of copper atoms in the ore Until the Harvard experimental results were announced, this atomic weight was represented as 63.2, whereas the experiments showed the figure to be 63.6. Evidently this difference of two-fifths of one percent means an increase in value to the seller of about $4000 on one million dollars worth of ore." Unfortunately for the moral, copper is usually determined electrolytically and the amount of copper found is therefore absolutely independent of the atomic weight. If this line of argument were pushed to the extreme, we should probably be told that if a daring scientist should change the atomic weight of carbon, he would increase the B. T. U.'s in a ton of coal. *Wilder D. Bancroft*

A COMPARATIVE STUDY OF FRACTIONATING STILL-HEADS.[1]

BY NEIL PRESTON MOORE

Introductory and Historical

When a binary mixture is distilled from a distilling flask with a straight narrow neck, the separation of the two components in one distillation of the mixture is small, unless the boiling points of the substances are widely different, so that in order to obtain a good separation, a long series of systematic fractionations is necessary. If the boiling points of the components lie close together, the number of fractionations, the time consumed, together with mechanical losses and those by evaporation, contribute to the difficulty of separating the substances satisfactorily.

The object of this investigation was to determine the factors which it is necessary to control, in order to effect a better separation of the components of a mixture in a single distillation. It is not the purpose of the author to develop the subject theoretically but to employ the factors ascertained in the design of a still-head in which distillation can be conducted in the laboratory at a reasonable rate with a maximum efficiency of separation.

Many investigators, from time to time, have studied the problem with the view of improving the sharpness of separation of two liquids in a mixture by means of specially designed distilling heads, and various types have been offered, for some of which high degrees of efficiency are claimed. That the subject merits further study, is obviously shown in a recent article by J. Friedrichs,[2] in which he submits the comparative efficiencies of various still-heads now used in common practice. A short review, perhaps, of the work of this character that has been done in the past, will be in order. The

[1] A thesis submitted to the Faculty of Leland Stanford Junior University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

[2] J. Friedrichs: Zeit. angew. Chemie, 1, 32, 340 (1919).

subject naturally divides itself into two well-defined parts: still-heads without temperature control (A) and those in which the temperature is regulated (B).

A. Still-Heads without Temperature Control

Wurtz[1] in order to separate butyl alcohol from fusel oils, recommended the employment of a still-head consisting of a vertical tube with two bulbs blown in it. The less volatile constituents of the mixture were supposed to condense upon the sides of the bulbs, and run back into the flask.

Linnemann[2] introduced an essential improvement to the Wurtz head, by placing small bowls of platinum gauze above one another within the tube. He suggests in his article, the necessity of the dephlegmating effect upon the hot vapors by the condensed liquid. Various improvements have been made, from time to time, namely, Belohoubek,[3] who by a simple device removed the tendency of the condensed liquid in the head to regurgitate.

Glinsky[4] devised an apparatus which embodied both the bulb features of the Wurtz head and the platinum gauze bowls of the Linnemann design.

The still-head of Le Bel-Henninger[5] was constructed according to the same principle.

Hempel[6] recommended the use of a column filled with glass beads, to serve as a fractionating head. The inclusion of a large amount of reflux liquid by the heads is an objection to the use of the head for small quantities of liquids.

Other modifications of still-heads have been proposed by Sidney Young[7] such as the "Rod and Disc" and the "Pear" types.

The "Rod and Disc" form consisted of a long tube

[1] A. Wurtz: Liebig's Ann., **93**, 108 (1854)
[2] Linnemann: Liebig's Ann., **160**, 195 (1871).
[3] Belohoubek: Zeit. anal. Chem., **20**, 517.
[4] Glinsky: Liebig's Ann., **175**, 381 (1875)
[5] Ber. deutsch. chem. Ges., **7**, 1084 (1874).
[6] Hempel: Zeit. anal. Chem., **20**, 502.
[7] Sidney Young: Jour. Chem. Soc., **75**, 679 (1899).

through which passed a central rod bearing discs at suitable intervals. This arrangement was designed to retard the backward flow of the condensed liquid and to create eddies and cross currents in the vapor phase.

The "Pear" head was a modified type of the Wurtz bulb apparatus. The bulb was telescoped slightly at the top, so as to give it a pear-like shape. The advantage of this modification was to prevent the condensed liquid, after flowing down the constrictions in any bulb, from spreading over the surface of the bulb below, mixing with the liquid in that bulb, and flowing down the sides with a much greater velocity. Instead, the liquid collected upon the end of the depression, and dropped directly into the center tube of the head. The peculiar shape of the tube may have caused more eddies of vapor than is possible in other forms of bulb heads.

The Young and Thomas[1] tube has been described by them in connection with the separation of hexanes from American petroleum. The dephlegmator consisted of a long glass tube 17 mm in diameter, provided with a side delivery tube. Concave rings of platinum gauze fixed in the tube by a constriction supported small glass reflux tubes to accommodate the condensate.

Recognizing the need of reducing as far as possible, the amount of reflux liquid in the still-head, led Young[2] to devise a form of apparatus known as the "Evaporator." This device was designed so as to reduce to a minimum the amount of condensed liquid, and at the same time secure thorough contact between the liquid and vapor.

In the general form of the apparatus, each section consisted of three separate parts, an outer tube or jacket, which is connected to the other sections, a thin-walled tube open at each end, and an intermediate tube, which fitted over a second like an inverted test-tube. Attached to the top of the inverted tube, by means of three legs, is a small funnel-like device which served to collect the condensed liquid flowing downward

[1] Young and Thomas: Chem. News, 71, 177 (1895).

[2] Loc. cit..

from the section above, and to redistribute it over the surface of the inverted tube. In this style of apparatus, the vapor is compelled to take a very circuitous path and excellent contact of the vapor with the liquid is claimed.

Young made a comparative study of the efficiencies of all the still-heads that have been previously mentioned. The "Evaporator" form was the most efficient of all except the Hempel column. The Young head, however, has the advantage of retaining but two-thirds as much liquid as the Hempel type.

B. Controlled-Temperature Still-Heads

The first investigator to employ a regulated still-head was Warren de la Rue[1] who endeavored to separate liquid mixtures whose boiling points lie close together, into their respective components. He says, to quote his own words, "Der Verfasser hat daher einen neuen Apparat construirt, welcher sich hauptsächlich dadurch von den bisher gebräuchlichen unterscheidet, dass man die Temperatüre der übergehenden Dämpfe genau controliren, und sie dann schnell auf die Temperatur abkühlen kann, bei welcher die sehr flüchtige Körper noch in Dampfzustande beharren."

The procedure of de la Rue consisted in passing the vapors of the mixture to be distilled upward through a worm tube of copper. The tube was placed in a bath whose temperature was maintained by a special lamp and oven. The bath contained water, oil, molten metal or whatever was necessary to maintain the required temperature. For temperatures below those of the room, provision was made for the use of different freezing mixtures.

The experiments of de la Rue were confined to liquids whose boiling points lie from 20° to 30° apart and some of which formed constant boiling mixtures.

Winssinger[2] raised the objection that the still-head of de la Rue was not applicable for the fractionation of small quan-

[1] Warren de la Rue: Zeit. anal. Chem., 4, 243 (1865).

[2] C. Winssinger: Ber. deutsch. chem. Ges., 16, 2641 (1883).

tities of liquids, and also that he had attempted to fractionate only by complete condensation at a fixed temperature. The apparatus of Winssinger made use of the complete condensation feature, but in addition made provision to introduce continuous contact between the ascending vapor and the descending liquid in the still-head.

Winssinger passed a current of water at constant temperature through a double tube placed inside of a vertical still-head. The vapors were allowed to pass through the annular space between the water tube and the outside wall. No other provision was made to bring about the "washing" effect other than the condensation of the vapors on the sides of the tube. Very good separations, however, are claimed by the investigator.

Claudon[1] improved Winssinger's apparatus by surrounding the inner tube with copper gauze.

Frederick D. Brown[2] devised an arrangement by which he endeavored to eliminate the refinements of temperature regulation that were necessary in the apparatus of the preceding men. His scheme was to heat a spiral head by means of a suitable liquid boiling under reduced or atmospheric pressure as convenient. While Brown believed that his separations were more or less independent of the "washing" effect, it is nevertheless certain that some "washing" effect would be obtained in a simple worm tube. Brown claimed his experiments showed that when the still-head is maintained at the boiling temperature of the most volatile component of the mixture distilled, that substance alone or nearly alone will pass over.

Young and Thomas[3] employed a combination of a regulated still-head with a dephlegmator, in order to separate normal and iso-pentane in a pure state from the light fractions of American petroleum.

The regulated head devised by them consisted of a tin

[1] Claudon: Bull. Soc. chim. Paris, **42**, 613 (1884).
[2] F. D. Brown: Jour. Chem. Soc., **37**, 49 (1880).
[3] Young and Thomas: Jour. Chem. Soc., **71**, 440 (1897).

worm tube enclosed in a well-regulated water bath. The temperature of the water bath was not kept constant for any considerable length of time, but allowed to rise very slowly as the distillation proceeded. No other details are given concerning the operation of the still-head.

In an investigation of partial pressures of binary mixtures, Rosanoff, Lamb and Breithut[1] employed a constant temperature still-head, in order to produce vapors having a perfectly constant composition. Their method was practically that used by Brown. The success of the method depended to a large extent upon the form of head employed. Numerous forms of this type were tried and a form capable of a variety of uses was described.

The distilling head consisted of a double-walled cylinder of metal, open at each end, and immersed in a suitable liquid bath maintained at constant temperature. The equilibrium chamber was furnished by the annular space between the two metallic walls of the cylinder. The lower outlet was connected with a flask containing the mixture to be distilled, while the delivery tube at the top was connected to a water cooled condenser.

Rosanoff and his colleagues claim a good efficiency for this type of still-head. A mixture of carbon tetrachloride and toluene containing 72.5 and 27.43 percent, respectively, was distilled at a temperature varying between 78.9° and 79°. The vapors in four fractions were found to contain an average percentage composition of 93.03 carbon tetrachloride. At the end of the distillation, the percentage of carbon tetrachloride in the flask had fallen from 72.5 to 56.2. Several other experiments are quoted which gave comparable results.

The conclusions arrived at by Brown,[2] and Rosanoff, Schultze and Dunphy[3] showed that if a mixture is distilled through a constant temperature head, the composition of the distillate is the same as that of a vapor evolved by a mixture

[1] Rosanoff, Lamb and Breithut: Jour. Am. Chem. Soc., **31**, 454 (1909).

[2] Loc. cit.

[3] Rosanoff, Schultze and Dunphy: Jour. Am. Chem. Soc., **37**, 1072 (1915).

whose boiling point has the same temperature as the still-head. The composition of the distillate of binary mixtures is constant at constant temperature.

A comparative study of fractionating heads has been recently made by J. Friedrichs.[1] A mixture of equal volumes of benzene and toluene was used in the distillations. The curves of total volatile distillate vs. temperature were compared. The sharpness of separation obtained by means of the different columns used resulted in a classification in the relative order of their efficiencies.

(1) Hempel[2] 58 cm (a column surrounded by boiling toluene), (2) Modified Plücker,[3] (3) Plücker,[4] (4) Winssinger[5]-Hempel, (5) Hempel[6] 30 cm, (6) Golodetz,[7] (7) Hempel[8] 2.8 cm, (8) Norton and Otten,[9] three-bulb, (9) Le Bel-Henninger,[10] three-bulb, (10) Linnemann,[11] three-bulb, (11) Glinsky,[12] three-bulb, (12) Wurtz,[13] two-bulb, (13) the ordinary distilling flask.[14]

Choice of Substances and their Properties

The substances chosen for this investigation were the organic liquids choloroform and carbon tetrachloride.

The reasons for the choice of these materials were first: No one of their mixtures is constant boiling. Secondly, the differences of their refractive indices made them amenable to convenient analysis by the refractometric method. The analytical procedure will be described later in the paper.

[1] J. Friedrichs: Zeit. angew. Chemie, 1, 32, 340 (1919).
[2] J. Friedrichs: Loc. cit
[3] Plücker: Chem. Ztg., 37, 1441 (1913).
[4] Ibid.
[5] Hempel: Loc cit.
[6] Ibid.
[7] Golodetz: Jour. Soc. Chem Ind, 31, 304 (1912).
[8] Hempel: Loc. cit.
[9] Norton and Otten: Am. Chem. Jour., 10, 62 (1888).
[10] Le Bel-Henninger: Loc. cit.
[11] Linnemann: Loc. cit.
[12] Glinsky: Loc. cit.
[13] Wurtz: Loc. cit.
[14] Commanducci: Chem. Ztg., 35, 706.

Thirdly, their boiling points lie sufficiently near together to render their separation rather tedious by the ordinary methods of fractional distillation. The chloroform used in this work was, "Baker's Analyzed U. S. P." and "Hercules," a product sold by Braun-Knecht-Heimann Company, of San Francisco, California. These samples each contained 0.6 to 1 percent ethyl alcohol to prevent hydrolysis.

To remove the alcohol, portions of about 500 cc of chloroform were shaken repeatedly in a separating funnel with C. P. concentrated sulphuric acid. Upon standing a short time, after each treatment, the acid was carefully drained off. This operation was repeated until fresh additions of acid were not discolored. The washed chloroform was then allowed to stand over night in the separating funnel, in order to permit more of the sulphuric acid to settle out. When the acid was completely drained off, the purified liquid was transferred to a clean dry bottle containing about 500 grams of unslaked lime. This treatment yielded a product which had a constant boiling point of 61.2° at 763 mm and a constant index of refraction for the D line of sodium which agreed to within 0.06 percent of the value given for pure chloroform in Landolt's Tabellen.

The function of the lime is two-fold. By its presence any amount of sulphuric acid remaining in the chloroform is neutralized, and the water liberated in the reaction of the lime and sulphuric acid will be reacted upon by the excess of lime and removed. This is a matter in which the methods of purification at first employed gave rise to some difficulty. In the earlier attempts at purification adopted, the last traces of sulphuric acid were removed by milk of lime and the final drying accomplished by means of anhydrous calcium chloride. The chloroform subjected to this method of purification, invariably hydrolyzed. However, it was found that, after treatment with sulphuric acid, chloroform free from the presence of substances usually added to prevent hydrolysis, may be preserved indefinitely over quick lime.

The carbon tetrachloride used in this investigation was of

two sorts, "Baker's Analyzed," C.P., and a product manufactured by Bausch and Lomb. A preliminary distillation of those liquids indicated that further purification was necessary. The procedure was exactly the same as that used in the case of chloroform. In the fractionation of carbon tetrachloride, all fractions below 76.7° (the boiling point of carbon tetrachloride), were rejected. The remaining fractions were collected and redistilled until they showed the same index of refraction. The refractive index of the purified material was the same as that of Kahlbaum's C.P. carbon tetrachloride.

Method of Analysis

The analyses of the liquid mixtures were carried out by means of the refractometric method. The instrument employed was the Pulfrich model (New construction) manufactured by Zeiss.

The procedure used was a modified form of an analytical-graphic type originally recommended by Ostwald and employed by von Zawidski[1] in his classic contribution, "On the Partial Vapor Pressures of Binary Mixtures." Rosanoff and Eastley[2] modified the method further and introduced an interpolation scheme.

The measurements of the previously mentioned investigators were made by the aid of the refractometer at constant temperature. In the course of the present investigation, it was found that the temperature control of the liquid to be measured, and that of the prism in the instrument was very uncertain and difficult. Decision was made, on this account, to avoid, if possible, any necessity for temperature control in these measurements. The method used was as follows:

(1) A stable non-volatile liquid was chosen for a comparison substance. On account of its low volatility at ordinary temperatures, and its extreme stability on exposure to the air, white paraffine oil was found to be in all respects satisfactory.

(2) The temperature coefficient of the refractive angle

[1] Von Zawidski: Zeit. phys. Chem., 35, 129 (1900).

[2] Rosanoff and Eastley: Jour. Am. Chem. Soc., 31, 953 (1909).

of the oil was carefully determined within the possible range of temperature of the laboratory by allowing the liquid to warm up in the refractometer cell with the rise of temperature of a very slowly heated room. With the aid of an accurate thermometer immersed in the liquid to be measured, the refractive angle was recorded at every half degree rise in temperature. The total time consumed to heat the room from the initial temperature to that of the final reading was six hours.

(3) The temperature coefficients of carbon tetrachloride and chloroform were also accurately determined, in the same manner as that of the paraffine oil, over the same range of temperature.

(4) The refractive angles of nine known mixtures were accurately determined at room temperature, and, at the same time, a reading of the refractive angle of the oil in temperature equilibrium with the mixture was taken. This served to determine the temperature. The employment of a divided cell in the refractometer made a comparison determination of this character possible.

(5) The assumption was made that the temperature coefficients of the refractive angles of the mixtures was the average of that of their components in proportion to their content in the mixture. Since the temperature coefficients of the pure liquids were so nearly equal, it is not believed that any considerable error is introduced by this assumption.

The method of plotting the data thus obtained was as follows:

(1) The curves representing the temperature coefficients of the refractive angles of pure carbon tetrachloride, chloroform and paraffine oil were plotted on the same set of coordinates and on the same scale (Fig. I). The temperatures were taken as ordinates and the corresponding refractive angles as abscissae. Curve 1 (Fig. I) represents the temperature coefficient of the refractive angle of paraffine oil, curve 2 that of carbon tetrachloride and curve 3 that of chloroform.

(2) On this same graph the point was found correspond-

ing to the refractive angle of each of the known mixtures and its temperature as given by the oil reading.

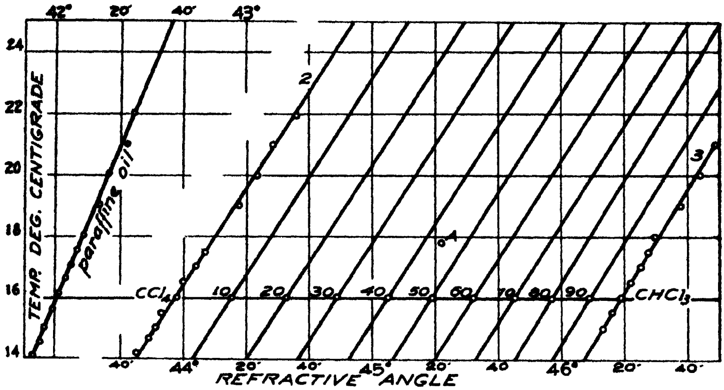

Fig I

(3) Then, on the basis of the assumption made in (5) above, the line representing the temperature coefficient of the refractive angle of each known mixture must divide all horizontal lines between the carbon tetrachloride and chloroform curves in the same ratio as that horizontal line on which the point lies is divided by this point. It is thus a perfectly simple matter to lay off these curves for all known mixtures for the temperature range over which the measurements extend.

From the above data, another curve (Fig. II) was then

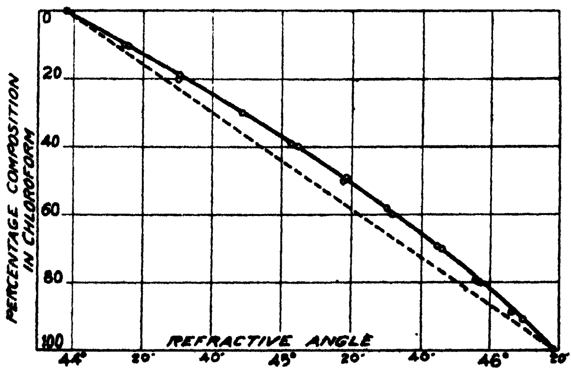

Fig. II

plotted on a new set of co-ordinates and to a different scale. The percentage composition by weight of the liquid mixtures whose refractive angles were determined in (4) above, served as ordinates while their corresponding refractive angles at 16° C were taken as abscissae. For the sake of easy reference in computing the analyses, it was deemed preferable thus to plot the refractive angles against composition at an arbitrarily chosen temperature rather than to attempt to incorporate a composition axis in the temperature—refractive angle system. By the aid of this curve, if the refractive angle of any possible mixture of carbon tetrachloride and chloroform is known at 16°, the percentage composition of the mixture may be directly ascertained from the ordinate.

In order to explain the use of this analytical scheme, the analysis of an actual mixture of carbon tetrachloride and chloroform will be cited as an illustration. A certain mixture gave a refractive angle of 45° 22′ while that of the oil measured immediately after at the same temperature was 42° 8′. By referring to the oil curve(Curve 1, Fig. I), the temperature of the mixture was found to be 17.8° C at the time of the reading. The point A is then found between the carbon tetrachloride curve and that of chloroform (Fig. I) which corresponds to the refractive angle of the mixture and the temperature at which the angle was recorded. By scaling down the temperature coefficient curve corresponding to the mixture in question, the refractive angle at 16° is read directly as 45° 11′. Reference is then made to the refractive angle-percentage composition curve (Fig. II) and the percentage composition by weight corresponding to a mixture with the given refractive angle is found to be 44 percent chloroform and 56 percent carbon tetrachloride.

This method of analysis is very convenient and rapid. It is accurate, in the case of the particular pair of liquids studied, to ±1%. If the refractive indices of the components of any liquid mixture lie farther apart, the experimental error is correspondingly reduced. The variation of percentage composition of the substances in the mixture is

1% per minute of the refractive angle determined. The limit of accuracy to which the refractometer scale can be read is ±1 minute.

Experimental

It became apparent after a survey of the literature which has been reviewed in the historical section of this paper, that certain factors which are supposed to have a marked influence upon the sharpness of separation of liquid mixtures must be more definitely studied, in order to make an intelligent application of them to the design of a still-head.

Decision was made, on this account, to at first restrict the investigation to the simplest possible case, the plain vertical still-head, and then to submit modifications of this form to a comparative study. In order to make such a comparison, all distillations were made with mixtures of the same composition and volume, and at the same rate. The volume of the mixtures was four hundred cubic centimeters. The mixture chosen was 75 percent chloroform and 25 percent carbon tetrachloride. Realizing that the rate of distillation influenced greatly the composition of the distillate, the speed of distillation was maintained as nearly constant as possible. The rate employed in this work was two cc per minute, unless otherwise stated.

The distillate was collected in thirteen fractions of twenty-five cc each, the remaining seventy-five cc being considered as residue. The composition of the fractions is stated in percentage by weight of the components. The temperature of the vapors passing from the still-head was recorded at the time when each fraction began to come over.

The following forms of still-heads were studied more or less exhaustively.

A. The Plain Vertical Still-Head

1. Plain Distilling Flask.
   (*a*) With uncontrolled condensation in the neck.
   (*b*) With controlled condensation in the neck.
2. Empty Vertical Tube.
   (*a*) With uncontrolled condensation.

(*b*) With controlled condensation.
(*c*) As a constant temperature still-head.
(*d*) Head progressively heated during the course of the distillation.

B. With Wire Gauze in the Tube

1. With uncontrolled condensation.
2. With controlled condensation.
3. As a constant temperature still-head.
4. Head progressively heated during the course of the distillation.

C. With Rod and Cup Dephlegmator

1. With condensation uncontrolled.
2. With condensation controlled.
3. As a constant temperature still-head.

The Plain Vertical Still-Head

Plain Distilling Flask.—Two distillations were carried out under identical conditions, one in which the condensation of the vapor was permitted in the straight neck of the flask, while in the other, the neck was heated by passing an electric current through a number of turns of Ni-chrome wire wrapped around it. By means of this device, the condensation of the vapors in that region was entirely prevented.

As was anticipated, the best separation was obtained when the vapor was allowed to condense on the surface of the neck. Although nearly the whole degree of separation obtained was no doubt due to evaporation of the liquid from the surface of the mixture in conformity with the law of partial pressures, yet a noticeable improvement in the separation of the mixture into its respective components was noted, when condensation in the neck was permitted. This probably merely indicated that a certain amount of "dephlegmating" effect is produced by the small amount of condensation occurring in the neck under these conditions.

Empty Vertical Tube.—For a vertical still-head, a section of brass tubing five-eighths of an inch in diameter and thirty-six inches in length was employed. A side tube, one-fourth

of an inch in diameter, soldered firmly at the top of the long pipe, served to conduct the vapors to a water-cooled worm condenser. A thermometer, graduated in tenths of a degree, was inserted just opposite the vapor delivery pipe. This same thermometer was employed in all the still-heads used throughout the investigation.

Two experiments were performed in this type of head, (*a*) one in which the bare tube was exposed to the surrounding air, and (*b*) one in which the tube was well insulated against the conduction and radiation of heat.

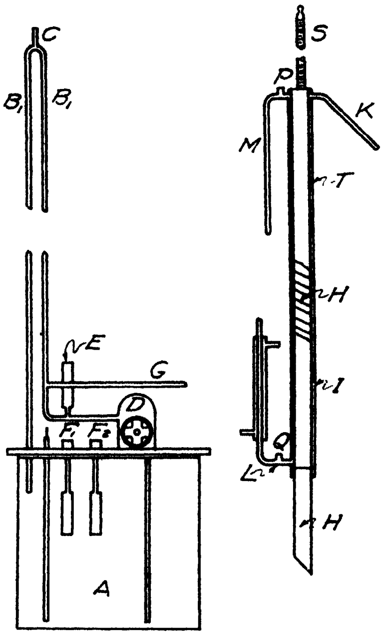

Fig III

As in the previous experiments with the plain distilling flask, the better separation was effected in the tube in which the greater condensations of vapors were allowed to take place.

For the purpose of comparison, the plain head was used as a constant temperature still-head. The construction of the apparatus is illustrated in Fig. III. The apparatus consisted of three parts, the constant temperature still-head, the hot water circulation system and the flask which contained the mixture to be distilled. The arrangement of the apparatus was such that hot water, which served the purpose of temperature regulation, could be pumped from heater A, and delivered to the still-head jacket at approximately constant temperature.

The regulated head was composed principally of an equilibrium chamber H, and a jacket I, through which water at constant temperature was circulated to provide the proper

temperature of the head. A piece of thin brass tubing H, thirty-six inches in length and five-eighths inches inside diameter served as an equilibrium chamber for the vapor and the condensed liquid. The outside surface of the tube was wound spirally with one-sixteenth inch copper wire, at a definite pitch, which was then soldered firmly in place. Another thin brass pipe I which fitted snugly over the wound wire extended to within three inches of the lower end of the tube H. This portion of the inner pipe was left exposed, in order to permit the attachment of the flask containing the distilling mixture. The annular space T between the tubes, when closed at the ends, formed the water jacket of the apparatus. Side tubes M and L made up of one-quarter inch brass tubing and provided with thermometer wells P and Q, were introduced into the jacket at the extreme ends of the column. A short brass tube K, the same size as the side tubes, was also placed at the upper end of the head, just opposite the point at which the tube M entered the still-head. This pipe, which passed through both walls of the jacket into the equilibrium chamber, served to conduct the vapors from the still-head into the condenser. The hot water (which maintained the temperature control of the still-head) was introduced through M, and by means of the spiral in the jacket, was caused to circulate around the periphery of the inner tube and to discharge through L back into the heating tank A. U was a cooler for the purpose of keeping the discharged water from the still-head below the temperature of the thermostat. In order to indicate the boiling point of the distillate, a thermometer S, graduated in tenths of a degree, was tightly fitted in the upper end of the equilibrium chamber.

The hot water circulation device included the following parts: A metal tank A well insulated with felt, which had a capacity of about twenty litres, a three-quarter inch all-bronze gear pump D, and a stand pipe fourteen feet in height, B_1B_2, made up of three-eighth inch galvanized iron pipe. An air chamber E between the pump and the stand pipe minimized the pulsations produced by the pump. The pump, air

chamber, and stand pipe were well protected against heat losses by a thick covering of magnesia packing. The water in the tank was heated by means of electric immersion heaters F_1 and F_2. The temperature was maintained constant to within 0.3° C with the aid of a regulating arrangement.

The hot water was continuously pumped over the stand pipe B_1 past the air vent C_1 at the top of the column and allowed to flow back through B_2 by gravity into the heating tank A where it was again available for use. The water necessary to preserve the temperature of the still-head was taken from the stand-pipe B_1 at a point about one foot above tank A by means of pipe G.

The vessel which contained the mixture to be distilled was an ordinary 500 cc balloon flask with a short neck. The contents of the flask were heated with direct current at forty-eight volts and giving one to three amperes. The heating element consisted of an electric immersion heater, composed of a coil of Ni-chrome wire of about twenty ohms resistance. The coil was connected between two leads of heavy copper wire which were passed through the cork stopper of the flask and connected to the source of electricity. The amount of current supplied to the heating coil of the flask was controlled by an outside variable resistance. The distillate was collected in a 50 cc graduated cylinder which was fixed tightly to the adapter of an ordinary Liebig condenser.

In all joints, where it was necessary to prevent leakages of the distilling mixture, the use of Le Page's glue was found to be in all respects satisfactory. Neither chloroform nor carbon tetrachloride affect this particular glue in any manner.

While the constant temperature head (see Table I) gave more effective separations than any of the modifications of the plain head used heretofore, it has, however, certain serious disadvantages. Firstly, the sharpness of separation is limited to the degree of accuracy to which the temperature of the head can be controlled. Secondly, it is very difficult to regulate the temperature of the bath, and at the same time supply

heat to the distilling mixture at such a rate as to preserve a constant flow of distillate.

The rate of distillation possible in a constant temperature head depends upon the amount of low boiling vapor that can be forced into the still-head from the mixture. In the distillation of a mixture of carbon tetrachloride and chloroform containing seventy-five percent of the latter, not more than half of the chloroform can be obtained at a constant temperature held only slightly above that of the boiling point of chloroform. At this point, the distilling mixture is so impoverished of the low boiling component that one is unable to crowd enough of the low boiling vapor into the still-head to preserve the rate of distillation without forcing the mixed vapors into the condenser before equilibrium conditions are established. In other words, with this form of apparatus, one is forced to a very slow rate of distillation in order to get much efficiency.

It was thought that perhaps this difficulty might be eliminated, and yet a fairly satisfactory separation be obtained if the temperature of the bath was allowed to slowly rise during the course of the distillation and the amount of heat supplied to the distilling mixture kept the same. An experiment was accordingly made in which the temperature of the bath was allowed to increase at a rate of four degrees per hour. This supply of heat insured a distilling rate of approximately two cc per minute throughout the whole distillation.

The degree of separation of the components of the mixture was about the same as that obtained in the experiment with the plain distilling flask with the heated neck, or in which condensation was eliminated.

In order to give a more definite idea of the relative efficiencies of the forms of apparatus thus far studied, the results of these distillations are represented in the table below. The numbers represent the average percentage of chloroform in the first four fractions collected. While complete analysis of all fractions was made, and corresponding tables of data are available, it seems more or less superfluous to publish them.

In almost all cases the composition of the first four fractions was so nearly identical that it is believed that the average composition of these fractions gives in all cases a very fair estimate of the efficiency of separation obtained.

TABLE I

1. Plain distilling flask—condensation uncontrolled	84.6
2. Plain distilling flask—condensation controlled	81.4
3. Simple brass head—condensation uncontrolled	85.2
4. Simple brass head—condensation controlled	84.4
5. Constant temperature head at 62.1°	89.5
6. Temperature of the bath allowed to rise during the course of the distillation	81.4

Experiments with Gauze in the Tube

The inner space of the plain brass tube was completely filled with tightly rolled copper gauze. The gauze was rolled upon a quarter inch iron rod and securely soldered at each end. The iron rod formed a core for the rolled gauze so that no chimney might be left in the center. The still thus modified was subjected to the same experimental tests as the plain vertical tube. The following table gives the relative efficiencies of the gauze under the various conditions studied.

TABLE II

1. Entire head kept above the boiling point of CCl_4	81.4
2. Condensation in the head uncontrolled	90 0
3. Condensation in the head controlled	90.0
4. As a constant temperature head at 62°	90.3
5. Temperature of the bath allowed to rise during the course of the distillation	82.7

As in the previous case of the plain brass still-head, the constant temperature head, as far as it was able to operate, yielded the best results. The difference in the efficiencies between the controlled and the uncontrolled modifications of the same type of head are the same. In every experiment, however, in which the gauze has been used, a marked improvement in the completeness of separation can be observed.

Experiment with the Rod and Cup Dephlegmator

In order to complete the comparative study of the various forms of apparatus and to introduce a form of dephlegmator

used by previous investigators, it was decided to submit the rod and cup design to the same experimental tests as were used in connection with the gauze.

The dephlegmator which was chosen to serve the purpose consisted of a series of shallow brass cups held in position by a central rod of the same material. The cups were stamped out of thin sheet brass by a die made especially for the purpose. The diameter of the cups was one sixty-fourth of an inch less than the inside diameter of the still-head. This difference in dimension permitted the easy insertion and withdrawal of the dephlegmator from the still-head tube. Around the edge of each cup, four small notches were cut at equal distances apart to allow the condensed liquid to flow down past the cup and at the same time permit the ascent of the hot vapors. Over the lower fourth of the tube, the notches were gradually enlarged toward the bottom so as to prevent regurgitation of the condensed liquid. The cups were tightly soldered to the rod at intervals of one-half inch.

The following table shows that the efficiencies of both the controlled and uncontrolled forms of this device are less than that of the still-head in which the gauze is used. The constant temperature form, however, gave a decided improvement in the separation of the mixture. With this apparatus it was, however, found impossible to maintain anything like the desired rate of distillation for more than four to six fractions. For this reason this type of still-head will not be further considered in this paper.

Table III

1. Condensation in the head uncontrolled	89.1
2. Condensation in the head controlled	88.7
3. As a constant temperature head at 62.2	92.3

PART II

Introduction

The investigation of the several types of still-heads which have just been described, and the impressions conveyed by a digestion of the literature on the subject in the historical

section of this paper, lead one to believe that much improvement may still be attained in the efficiency of distillation operations. An attempt will be made at this place to systematize the present knowledge of the subject with a view of cataloguing those factors which can be shown to be of influence in such operations as are under consideration, and then to proceed to devise some form of apparatus in which these factors may be satisfactorily combined.

General Theory

(1) What happens when a liquid mixture is distilled and the vapors are directly condensed? In this case, the efficiency is definitely limited by the partial pressures of the components and further separation is obtainable only by refractionation of the fractions already collected.

(2) The purpose of specially designed still-heads is always to give a greater degree of separation than is obtainable by the above method. The various factors which lead to this further separation seem not to be thoroughly understood. Two effects have, in general, been looked for in this connection.

(*a*) The phenomenon known as the "dephlegmating" or "washing" effect which is the name for what occurs when portions of oncoming vapor are brought into more or less intimate contact with the condensate in the still-head on its way back to the still. The essential thing involved here is a continual redistillation of the condensate, the necessary heat being taken from the oncoming vapors which are at a higher temperature. By this process, the higher boiling constituents in the vapor are being continually condensed, while the lower boiling constituents in the condensate are being continually vaporized, and a separation which is comparable to a repeated series of fractionations is obtained in one operation.

(*b*) The second effect which seems to be more or less tacitly believed to exist is as follows: It is assumed that if a quantity of vapor is passed through a tube of considerable length, a gradual but more effective separation is obtained than if the vapors are passed through a tube of shorter length,

and this more or less independently of any "washing" effect. While such an effect does perhaps exist, it has unquestionably been greatly exaggerated, and the improvement of separation effected by lengthening the still-head is already reached with relatively short lengths. As was noticed in the investigation of the constant temperature still-head in Part I, practically all of the condensation takes place within the lower fourth of the three-foot tube and the remaining portion of the tube is useless in so far as improving the efficiency of the head is concerned. A comparison of the efficiencies of the still-heads with controlled condensation with those of the distilling flask under the same conditions bear out the correctness of this conclusion. The degree of separation obtained from the head in which no condensation was permitted was the same as that from the distilling flask in which the temperature of the neck was so controlled that the separation obtained was directly due to the relative partial pressures of the components. In other words, whenever there is condensation taking place in a still-head, a certain amount of "washing" or "dephlegmating" effect is certainly present and it alone is probably responsible for any separation which occurs.

The possibility of such an effect as has been described and which is distinct from the "washing" effect, is based upon the assumption that the rate of deposition of the liquid from the mixed vapors is a slow one. All of the results obtained in this investigation seem to show that it is quite rapid, and that consequently any extension of the capacity of the still-head beyond a very modest limit is wholly unnecessary and probably disadvantageous. Everything seems to lead to the validity of the following principle: That, in order to obtain the greatest efficiency of separation at a given rate of delivery from the still, it is best to allow the temperature gradient along the still-head to establish itself naturally (*i. e.*, not to attempt any sort of *constant* temperature control) and to make the best possible provision for a maximum "washing" effect within the still-head.

(3) The purpose of fractional distillation can never be to

obtain "perfect" separation of two or more liquids, for while such a separation may be imagined, it implies an almost infinite nicety of regulation and equally great expenditure of time. Thus any practical device must be one that will deliver distillate at a "reasonable" rate. Consequently, it is never attempted to deliver vapor to the condenser at the temperature of the boiling point of the lower boiling component, but at a temperature always somewhat above that and corresponding to the boiling point of the richest mixture (with respect to the more volatile component) which it is possible to drive over at the desired rate.

(4) The problem thus narrows down to the designing of an apparatus in which the maximum opportunity is offered for repeated condensation and re-evaporation throughout the whole length of the still-head at a temperature gradient which establishes itself naturally when the still is operated for a certain rate of delivery. This implies a maximum amount of radiation (in order to furnish the maximum amount of condensate for redistillation) and a maximum amount of heat supplied to the still-head internally by the vapors from the still (in order to bring about the necessary partial revaporization of the condensate). With a still-head of given capacity, the limit of operation will be reached when internal disturbances such as regurgitation begin to take place.

(5) If the above principle is sound, it is easy to determine the main factors involved in putting them into practical operation, always having in mind that the purpose is to increase the efficiency of separation *when some definite rate of delivery is demanded.* These factors are as follows:

(*a*) The rate at which vapors are delivered to the still-head. Since they form the sole source of heat for the revaporization of the condensate, and consequently for refractionation in the still-head, this should be as great as the apparatus will stand without producing internal disturbances.

(*b*) The rate at which the vapors are condensed in the still-head. Since this rate determines the supply of condensate for the re-evaporation, it should be as rapid as possible.

This may be accomplished by increasing the radiation from the walls of the still-head, provided this is done in such a way as to not interfere with the maintenance of the desired temperature gradient within the head. It may also be pointed out that an increase in the rate of condensation (that is of radiation) will demand an increase in the rate at which vapors are introduced from the still in order to maintain the chosen rate of delivery to the receiver.

(*c*) The rate at which condensate returns to the still-head. This is a matter of very great importance, but one, however, which can be determined only by direct experiment. The most effective rate will probably be different in different cases. It is obvious that if the condensate be returned too rapidly to the still there will be comparatively little opportunity for re-evaporation and if it is to be returned too slowly much of the heat taken from the oncoming vapors will be lost in re-evaporating the higher boiling components. It is perhaps unnecessary to point out that with a constant rate of delivery to the receiver, any alteration in the rate of flow of condensate back to the still will be necessarily connected with a change in the rate of delivery of vapors from the still and consequently also with a change in the rate of radiation from the still walls.

(*d*) The effectiveness of the continual interchange of heat (and consequently of composition) between the oncoming vapors and the condensate within the still-head. There is involved here nothing more or less than the efficiency which may be given to the "washing" effect. This may be accomplished by various mechanical devices. These mechanical devices should aim to do two things: (1) To hold up in the still-head during the operation the most favorable volume of condensate; (2) to properly distribute it on its return flow.

(6) Aside from the factors already described there is another which is of great importance, but which seems to have received little or no attention up to the present time. This is the matter of localizing the radiation from the still-

head in such a way as to give the most effective results. It is perfectly obvious that since in the still-head it is vapor which is to be condensed and liquid which is to be evaporated, a considerable advantage is to be expected if things can be so arranged that the radiation takes heat, so far as possible, only from the vapor phase, leaving the liquid condensate at all times as hot as possible. If it be admitted that this principle is of importance (as it will be shown to be) it follows that the worst possible design of still-head is the open vertical cylindrical tube, for here the radiation from the walls causes practically all of the liquid to condense on their inner surfaces. Heat is thus abstracted from the vapors only secondarily. A considerable portion of it is used in warming up the over-chilled liquid to the temperature necessary for the satisfactory redistillation.

With the above principles in mind, the apparatus to be described was designed, in the hope that it would fulfill the desired conditions more satisfactorily than the usual form of still-head, or that it would at least make possible a systematic study of the practical value of these principles.

The Flat Still-Head

In casting about for some form of still-head that would fulfill the above conditions in the most satisfactory manner, it seemed wise to depart as far as possible from the conventional cylindrical model. In order to accomplish this, one is led directly to a form which is as much flattened as possible, and there follows a detailed description of the head which was actually constructed.

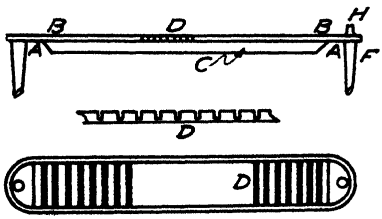

Fig. IV

The details of construction of the apparatus are illustrated by the drawing in Fig. IV. The apparatus was made entirely of brass. The dimensions of the still-head were: Length, thirty-six inches; width, six inches; depth, one-eighth inch.

A bed plate, A, one-sixteenth of an inch in thickness, and a cover plate B, one-half as thick, formed the bottom and top of the still-head. The thickness of these plates was purposely made different. A heavier grade of material was used in the bed plate in order to give the apparatus greater rigidity, while the truss C, was used for re-enforcement. A thinner piece of metal was used for the cover plate to increase radiation from that surface. The plates were rounded at the ends with a radius of curvation of three inches. On the surface of the bed were soldered one hundred and twenty slotted angle strips D, one-quarter of an inch apart. These angle strips were made of twenty-six gauge metal. One of them is shown in detail in Fig. IV. Each strip was six by three-sixteenths inches in dimension with a one-eighth inch "turn-up." This "turn-up" was provided with slots three-thirty-seconds of an inch in depth and one-thirty-second of an inch in width. By this arrangement, each strip constituted a dam, one-thirty-second of an inch in height, completely across the bed plate. The slots served as open sluices through which the over-flow liquid could travel down the head. At the same time, the upper ends of the teeth (i. e., the metal left standing between the slots), was of such height as to make close contact with the cover plate. In order to accommodate the continual increase in volume of condensate on nearing the still, the number of slots was increased progressively from the top to the bottom of the head. To accomplish this purpose, the strips were divided into eighteen sets of seven each. Each member of the first set contained five slots, this number being increased by five in each set thereafter. This arrangement gave the strips of the set at the lower end of the still-head ninety slots. The cover plate B, and the bed plate A, were joined together by a strip of one-eighth inch square rod, which ran continuously around the edge of the plates thus completing the boxing in of the apparatus. The plates were tightly soldered to the rod and to facilitate removal, the cover plate was fastened with a lower melting solder. A pipe E, five-eighths of an inch in diameter, was soldered into a hole at the

extreme lower end of the bed plate to receive the distilling flask. This tube was four inches in length and was flared at its junction with the bed plate, in order to prevent any accumulation of condensed liquid at that point. At the extreme upper end of the bed plate another pipe F, one-half inch in diameter and six inches in length served as a delivery tube for the vapors. This pipe was flared to five-eighths inches at the junction with the bed plate in order to provide more room for the thermometer bulb. To serve as a thermometer holder, a short piece of one-half inch tubing H, one inch in height, was soldered into a hole in the cover directly over the orifice of the delivery tube. This position of the holder permitted the bulb of the thermometer to extend to the exit point of the vapors. The same thermometer was used as in the previous experiments.

A still-head of this design affords the desired opportunity to study the effect of the various factors discussed above.

(*a*) The rate at which the vapors are delivered to the still-head may be varied as usual by variation of the current supplied to the electric heating coil in the still.

(*b*) The rate at which the vapors are condensed in the still-head may be varied by devices which aid or deter radiation from the surfaces.

(*c*) The rate at which the condensate returns to the still may be regulated by altering the slope at which the head is set during operation. Of course, this is the same thing as regulating the amount of condensate held up in the still-head during operation.

(*d*) The effectiveness of interchange of heat between the liquid and vapor in the still-head, while it is not subject to any particular regulation, should be always very high, as a result of internal construction of the head.

(*e*) The localization of radiation can also be accomplished in this form of still-head by simply insulating the bottom wall, thus forcing all radiation to take place from the top. While, of course, the liquid must largely condense on the inner side of the radiating upper wall, it will nevertheless flow as

rapidly as possible down the strips (whose teeth are in close contact with this wall), to the bottom wall, along which it will flow back to the still in such a way as to be protected from further loss of heat, on account of the insulation. The hot vapors will then always be giving up heat to the wall through the thinnest possible film of liquid.

Experimental

Several runs were made with this head. The same conditions as to the mixture distilled, its composition, volume and calculation of efficiencies were maintained as in Part I. On account of the fact, that a larger quantity of condensed liquid was held up in the flat still-head than in the other types used in Part I, eleven instead of thirteen fractions were collected. The twelfth fraction consisted of the residue.

The range of special conditions under which this head was studied was as follows:

A. The Plain Still-Head.—The first distillation in the flat head was made in the form in which it was received from the maker, no supplementary devices being added to improve its efficiency. The apparatus was operated at an angle of forty-five degrees.

B. Runs with Bed Insulated with Asbestos Paper.—The bed of the still-head was now well insulated against radiation of heat to the surrounding air. To accomplish this purpose, three layers of asbestos paper were pasted on the under side of the bottom wall of the apparatus. The top wall was left as before.

C. Runs with Insulation as Above and Additional Provision Made for Controlling Radiation.—(1) Coating the cover with lamp black. The cover of the apparatus was coated with lamp black, applied by holding the plate over a flame of burning benzene.

(2) Air cooling the cover to different degrees. In order to accomplish this purpose, a wood frame, the exact dimensions of the still-head cover, was constructed of thin pine strips. A sheet of cardboard, of the same dimensions, was glued to the frame and served as a top. This jacket was then

tightly clamped to the still-head cover. When the apparatus was in operation, a current of air, introduced through a small pipe at the upper end of the jacket, was continuously blown over the surface of the still-head cover and out through a large opening at the lower end. The air was introduced at three different velocities. At the lowest velocity, just enough motion was imparted to the air to overcome the convection currents due to the hot still-head cover; the highest velocity was the highest possible in the apparatus. The still-head was run at another velocity which was intermediate between those just mentioned.

D. Runs with the Still-Head at Various Slopes.—A series of distillations were made in which the still-head was inclined at angles of fifteen, thirty, forty-five, sixty and seventy-five degrees, respectively. These runs were made without any provision for air cooling.

A summary of results obtained from the operation of the flat still-head, under the various conditions described above, is shown in the following table, detailed data being omitted as in Part I, and only the efficiencies as calculated from the composition of the first four fractions being given. The apparatus was operated at an inclination of forty-five degrees unless otherwise stated.

Table IV

1. The plain flat still-head	94.4
2. The plain flat still-head with insulated bed	95.3
3. The flat still-head with insulated bed and lamp black on the cover	95.3
4. With insulated bed and air cooling to different degrees	
(*a*) With slow stream of air	94.4
(*b*) With intermediate stream of air	96.5
(*c*) With maximum stream of air	96.8
5. Run with insulated bed and lamp black on the cover. Apparatus operated at the following angles of inclination	
(*a*) Angle of inclination 15°	92.0
(*b*) Angle of inclination 30°	95.3
(*c*) Angle of inclination 45°	94.4
(*d*) Angle of inclination 60°	95.5
(*e*) Angle of inclination 75°	93.5

The results given in these tables may be briefly summarized as follows: When the plain flat still-head was used, the efficiency was far higher than that obtained in any form of still-head used in Part I, which is evidence directly favorable to the flat form even without any accessories. The slope at which the head is operated is immaterial within quite wide limits, but it may nevertheless be too great or too small. The results obtained by insulating the bed showed a notable improvement over the bare head. On coating the cover with lamp black, no improvement was shown in the separation of the mixture, probably due to the fact that any improvement in radiation was nullified by the increased insulation due to the lamp black deposit. In the remaining trials with the higher velocities of air, the apparatus gave the highest efficiency that has ever been obtained in this or any other type of still-head yet used by the author. It is quite possible that still further improvement might be attained by further development in devices for increasing radiation. Such work, however, was not undertaken.

Some idea of the magnitude of the efficiency increase due to this form of still-head may be reached by the following considerations:

(1) The minimum efficiency obtainable is that given by a distilling flask with the neck heated so as to prevent any condensation whatever. This gives 81.4 percent chloroform content in the first four fractions. A distillate of 100 percent chloroform content would represent perfect efficiency. Thus, the efficiency due to any particular type of still-head will be

$$\text{Efficiency} = \frac{100(x - 81.4)}{100 - 81.4} \text{ percent}$$

where x is the average percentage of chloroform in the first four fractions. The best results obtained with any cylindrical head without a dephlegmator was 89.5 percent chloroform, or an efficiency of about 43 percent. The best result in a cylindrical still-head with a dephlegmator was 90.3 percent or an efficiency of about 47.8 percent. The best result with the flat still-head was 96.8, or an efficiency of about 82.7 percent.

Summary

(1) A brief outline of the literature on the subject of laboratory still-heads is given.

(2) A method for the sufficiently accurate analysis of binary liquid mixtures by the refractometric method without the necessity for temperature control is described.

(3) An apparatus is described in which it was found possible to study the relative efficiencies of fractionation in a cylindrical still-head under a variety of conditions, and data concerning these efficiencies are given.

(4) These results, together with those obtained from a study of the literature, have made possible a practical analysis of the process of fractional distillation into certain factors which seem to be of primary importance.

(5) A second apparatus (the flat still-head) was constructed for the purpose of studying the influence of these factors.

(6) Working with this apparatus, under easily obtainable conditions, it has been found possible to increase the efficiency from the best obtainable with any type of cylindrical head studied (47.8 percent) to 82.7 percent.

This work was carried out at the suggestion and under the direction of Professor S. W. Young. The suggestions and kindly advice of Mr. W. E. Burke gave the writer much assistance in devising the method of analysis, and in conclusion, to him and particularly to Professor Young, the author acknowledges his deep indebtedness.

Stanford University,
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ON CHEMICAL AFFINITY

BY A. KOREVAAR

When we peruse the chemical literature and notice the meaning of the word affinity, it soon becomes clear that two different things are called by this name. In the first place, we know the classic definition of affinity coming from the Greek philosophers and which denotes a force, acting between combining atoms. In the second place, modern chemistry shows us the thermodynamical conception of affinity, created by van't Hoff, which defines affinity as the maximum external work done by the chemical reaction at constant temperature and volume.

We, therefore, find the chemists using two quite different definitions of chemical affinity. It is to be expected that such a state of affairs will cause a confusion in our science and this is really the case. The different text-books on chemistry define affinity quite differently. One maintains the classical definition, a second gives the thermodynamical one, and others mix both definitions up in a wonderful way, some even advocating removing this vague idea from chemical science.

This last would not be right. Neither the classical nor the thermodynamical conception is indefinite; but we must always remember that the word affinity denotes two quite different ideas. At present this is not generally known. This appears clearly from the confusion on this point, existing in our text-books, as shown by the following examples:

Lewis, in his "A System of Physical Chemistry," Vol. II, page 339 (1920), gives the definition by van't Hoff; Holleman, in his text-book of inorganic chemistry, page 47 (1906), the classical conception. Ostwald in his "Grundlinien der anorganischen Chemie," page 88 (1904), discusses the classical conception and advises not to use this idea, because he thinks it in contradiction with certain phenomena which, on page 104 appear to be the reversible reactions.

J. W. Mellor, in his "Modern Inorganic Chemistry," page 94, 1912, deals first with the classical conception, but does not stick to it further on, while R. de Forcrand in his "Cours de Chimie," 1919, does not speak at all about affinity.

Ostwald's attitude in his "Der Werdegang einer Wissenschaft," 1908, is quite remarkable. In this book, Chapter VI deals with affinity. In fact, in the beginning the author writes about affinity, but soon he enters into thermodynamical considerations without giving an analysis or description of the idea "affinity," and the reader gets the impression that the author does not know what he shall say on this point.

The cause of all this is quite clear. The authors are not conscious that two different ideas are called by the same name "affinity."

We hope that this short explanation may cause the different authors to revise their texts on this point and that they will not only rigidly separate the classical from the thermodynamical conception; but also that they will call these different ideas by different names. The best were perhaps to continue to call the classical conception by the name "affinity" and to denote the thermodynamical one by the maximum external work of the reaction.

O. Sackur[1] has contributed to a great extent to the existence of the above-mentioned confusion. His book on chemical affinity is well known and justly admired, as it gives a clear and simple treatment of the maximum external work and its applications to chemistry. But this author has totally forgotten that the classical conception of affinity has still a right to exist. Sackur begins in the first chapter with a historical development of the idea of affinity and we might expect that, in doing this, he would have discovered the confusion of ideas in question. But the author has failed to do so and therefore it is worth while to trace the historical line once more and show how it has been possible that chemical

[1] Dr. O. Sackur: Die chemische Affinität und ihre Messung. Vieweg (1908).

science gave birth to two different definitions of chemical affinity.

We may say that the conception of affinity as a force between the smallest particles, or in the middle ages, when the atomic theory was denied on the authority of Aristotle, as a force between the elements, remained invariably the same till the end of the 18th century. It is true that the nature of these forces was differently explained. The Greeks had an antropomorphistical conception of affinity and this character was preserved till the 17th century. The force, driving different substances together, was compared with love between two human beings. With the rise of the mechanical contemplation of nature in the 17th and 18th centuries the ideas on the nature of chemical force became more sober. Lemery (1675) thought the atoms were provided with little hooks for sticking to each other. Newton classified the chemical force under the gravitation of the smallest particles; but according to him it was not necessary that this force was, as with the visible masses, inversely proportional to the distance. This latter restriction was dropped by Buffon (1770) who saw no difference between chemical force and gravitation.

In all of these theories the driving force of a reaction was considered acting between the smallest particles of the combining substances. The difficulties arose when Berthollot proved experimentally that the progress of a reaction not only depends on the nature of the reacting substances but also on their quantity, or, as Guldberg and Waage proved afterwards, on their concentration. These researches led, in 1864, to the formulation of the law of mass action. Guldberg and Waage's views are of the greatest importance for our purpose and so we will pay some further attention to them.

Guldberg and Waage published their views in three treatises which are collected in Ostwald's Klassiker, No. 104, under the title: "Untersuchungen über die Chemischen Affinitäten." The treatises are dated 1864, 1867 and 1879, and we are not surprised that the ideas of the authors have

developed in that course of time. In fact, we shall see that their conception of chemical affinity has undergone radical changes. Their views may be summed up as follows:

A substance A and a substance B combine, by the operation of cohesive forces between the molecules, to a compound AB. When a substance C reacts with AB according to the equation

$$AB + C = AC + B,$$

then, AC is principally produced by cohesive forces between A and C. But the forces between A and B, and perhaps also between B and C, have all exerted their influence on the reaction, so that the force that finally produces AC is the result of the coöperation of different forces. This resultant force k is the coefficient of affinity. According to these investigators, the driving force of a reaction is not only proportional to the coefficient of affinity, but also to the concentrations of the reacting substances. While formerly only the affinity was considered to be the driving force of a reaction, according to the new conception, the affinity is only a part of the driving force. *The affinity has to be distinctly distinguished from the driving force of a reaction, they are quite different things.*

Guldberg and Waage expressed the driving force of a reaction by the product of the concentrations of the reacting substances and the coefficient of affinity k. When these concentrations are denoted by p and q, then the driving force = kpq. The authors originally thought that in determining k, they had found a measure for the affinity, for k was the resultant of the forces, acting between the molecules; but on this point they changed their views fundamentally. This appears from their treatise of 1879, where the idea of mobile equilibrium is developed in the following way:

To explain a reaction according to the equation:

$$A + B = A' + B',$$

it is insufficient to accept cohesive forces between the molecules, but it is also necessary to keep account with the motion of the atoms and molecules. The equilibrium is not a state

of repose, it is a mobile equilibrium, the reactions in both directions going equally fast. The authors give a sketch of a kinetical deduction of the law of mass action. If p and q are the number of molecules of A and B in the unit of volume, then the number of collisions between the molecules A and B is represented by the product pq. When each collision caused a reaction, the reaction velocity would be $= Qpq$, Q being a velocity coefficient, dependent on temperature. Of p molecules of A, only a part a will be in a condition to cause a reaction during a collision. Of q molecules of B, a part b is in a similar condition. So that ap molecules of A will combine with bq molecules of B, and the reaction velocity is: $Qapbq$ or kpq when $k = Qab$. It is clear that this formulation is based on a quite different conception of k. At present this constant k is the product of a velocity coefficient Q and two constants a and b, which are perhaps best called activity coefficients. For the present it is impossible to determine these constants separately.

Concerning their views on chemical affinity, we conclude from their treatises the following: Guldberg and Waage certainly adopt the classical idea of affinity, viz., the affinity being a force acting between the molecules. This is clear from their former treatise and appears in the mathematical treatment of the problem from the meaning of k. Their later considerations about the mobile equilibrium do not contradict the classical definition of affinity, but the meaning of k has become much more complicated and their conception of affinity is not clearly defined. The great importance of Guldberg and Waage's work does not lie in the sphere of affinity, and their great success is due to the formulation of the law of mass action, which became the basis of chemical statics and dynamics. At present, the names of these investigators are always connected with the law of mass action but never with chemical affinity, though this was originally the object of their researches.

Though they did not do it themselves, and though, as far as we know, others did not do it either, we may draw from

Guldberg and Waage's treatises a conclusion of importance. We have learned to make a sharp distinction between affinity as a force, acting between the smallest particles and the driving force of a reaction. This is clearly expressed in their original formula:

$$\text{Driving force} = kpq.$$

The driving force of a reaction is quite different from the affinity.

Though we are convinced that k is in some way connected with the affinity, it appears from the later treatise of Guldberg and Waage that this connection is not a simple one. It is true that they succeeded in determining k, but they did not know the exact meaning of k. This is the reason that all determinations of affinity have failed.

In 1883, van't Hoff showed that the driving force of a reaction can be measured by the maximum external work at constant temperature and constant volume which is done by the system in passing from the initial state to the equilibrium point. This thought has been of the greatest importance for chemical science, but it was a great pity that van't Hoff called the driving force a reaction, affinity[1] and in consequence, considered the maximum external work of a reaction a measure for affinity.

In the preceding pages we have emphasized the difference between the driving force and affinity. By calling the driving force, affinity, van't Hoff has made the clear distinction between these two different ideas very vague. This was unnecessary. The maximum external work is a sharply defined idea, which does not need any other name, and it was a pity, for it caused a confusion, which, as we have seen, remains in our text-books up to the present day.

After this digression we return to Sackur's historical treatment of affinity. Sackur did not understand the confusion of affinity and driving force. According to him, the thermodynamical conception of affinity has gradually developed

[1] Vorlesungen über theoretische und physikalische Chemie., 1, 171 (1901).

from the classical one. If this were true, the modern formulation would have made the ancient one superfluous, for then the modern one, by a broader development of the idea, would have opened an new insight given us a new viewpoint which would have included the old one completely. This did not happen and Sackur writes unjustly that van't Hoff succeeded in "*eine gluckliche Definition der Affnitatskraft aufzustellen, die allen bisherigen Erfahrungen Rechnung trägt und gleichzeitig die quantitative Messung in mechanischen Massen ermoglicht.*"

No, van't Hoff has mixed up the ideas of driving force and affinity; but, by calling the driving force affinity, the classical idea of affinity does not become superfluous. Therefore it is not true that van't Hoff's affinity, as Sackur says· "*allen bisherigen Erfahrungen Rechnung tragt.*"

It is better that the maximum external work of a reaction remains the maximum external work. Then, it is clear to everybody that the affinity is not meant. That is the question and as Sackur did not understand it, his much read and otherwise excellent book is also responsible for the confusion which prevails in this sphere of chemical science.

The Hague,
De ember, 1920

CONTRIBUTIONS TO THE STOICHIOMETRY OF ADSORPTION. I

ADSORPTION OF CATIONS OF THE ALKALIES AND ALKALINE EARTHS

BY SVEN ODÉN AND HUGO ANDERSSON

1. Introduction

(BY SVEN ODÉN)

In spite of the great number of researches dealing with adsorption and connected phenomena, amazingly little has been done to ascertain whether the quantities adsorbed by a given *adsorbent* are in any way related to the groups of elements within the *periodic system.* Thus, a great many writers have treated the question of whether adsorption is due to chemical or physical forces; but the stoïchiometrical point of view has hitherto been neglected. Though the investigations of H. Freundlich and his pupils show that certain groups, such as new fuchsine and morphine cations, are adsorbed in a specific way, the range of substances dealt with from this point of view by science is generally rather limited.

Although recent investigations have shown the inaccuracy of Freundlich's postulate, that equal quantities should be adsorbed from equimolar solutions, very little systematic work has been done with a view to determining *experimentally* how the adsorbed quantities vary with the cation if the anion of the salt is the same, or with the anion if the cation is unchanged.

The importance of this problem, especially for the phenomena of *coagulation*, has recently been dealt with in a paper by Wo. Ostwald,[1] though mainly by utilizing experimental work of previous investigators.

Some years ago the present author[2] showed that colloidal sulphur on coagulation by chlorides of the alkalies adsorbs

[1] Koll-Zeit., 26, 28, 69 (1920).

[2] Sven Odén: Der kolloide Schwefel. Pag. 136. Nova Acta Reg. Soc. scient. Ups., (4) 3, No. 4 (1913).

the same amount of Na, K, Rb, Cs, and Ba in the coagulate (in a special case 1.9 mole per 1000 g sulphur).

As the salt concentration in the dispersing medium that is required in order to coagulate varies as follows:

$$NaCl > KCl > RbCl > CsCl > BaCl_2$$
$$0.15 > 0.021 > 0.016 > 0.009 > 0.002 \text{ normal}$$

we may conclude that the salts with the lowest coagulating power must have been adsorbed most intensely, so that in this case, within the alkali group, the adsorption increases from sodium to caesium.

Some years after these investigations, an extensive series of observations was planned with a view to determining whether this regularity would also occur with other adsorbents, and to extend the research by a study of the influence of the anions. Thanks to the excellent instrument constructed for the measuring of slight variations of concentration by the Zeiss Company, viz., their interferometer, and with the aid of some younger scientists, I have succeeded in tracing some hundred adsorption isotherms with sulphur, charcoal, barium sulphate, ferric hydroxide, and humic bodies, as adsorbents.

In the present and following papers it is intended to describe some of these investigations, the observations on sulphur and humic bodies being reserved for special monographs. The main difficulties have arisen from the obstinacy with which the adsorbents have retained traces of impurities, especially hydrogen ions, which has led previous investigators to draw a great number of false conclusions.

A brief discussion of the so-called decomposition by adsorption, according to my opinion, caused by impurities in the adsorbents, will be found in Section 4.

2. Method of Measurements

As already mentioned, we have employed the Zeiss Interferometer, constructed by F. Löwe[1] from suggestions made by Lord Rayleigh,[2] in order to measure the difference of con-

[1] Phys. Zeit., 11, 1047 (1910). Zeit. Instrumentenkunde, 30, 321 (1910). Chem. Zeitung, Repetorium, 1910, 474.

[2] Proc. Roy. Soc., 59, 201 (1896); 64, 97 (1898).

centration between a solution of a given concentration, B, and a sample of the same solution, A, which has been shaken with the adsorbent (m) and from which in this way a certain amount (y) of the dissolved substance has been removed.

This sensitive instrument consists of two parallel sheets of glass, which by means of cross-sectional walls enclose two chambers, the whole being immersed in a cylindrical vessel filled with water to act as a thermostat. The light that traverses the chamber containing the original solution produces a system of interference bands by interference with the light that has passed through the other chamber, which is filled with the solution whose concentration has been lowered by the adsorption.

The distances passed through by the two rays differ optically by an amount *nearly, but not quite,* proportional to the difference of concentration, and there is a corresponding displacement of the intereference bands of zero order, compared with a fixed system of interference-bands. This displacement of the bands of the order 0 may be reduced to the initial position by means of a rotating plate of glass of the same type as the compensator of Jamin. The angle through which the compensator plate is turned (by means of a screw) should then be proportional to the difference in concentration, and previous authors have simply expressed the adsorbed quantity in scale units ("*Trommelteile*" = s. u.).

This relation between s. u. and differences of concentrations holds true only within very limited intervals. It has therefore been necessary to determine the concentration value (μ) of any s. u. for the different concentrations. This can be done in three ways:

1. We fill one compartment with pure water, the other with solutions of known concentration of the electrolyte in question, and plot the number of scale units (α) as abscissa against the concentration (c) as ordinate. We thus obtain curves (c,α) slightly concave towards the axis of the abscissae by means of which the actual concentration may be determined for the solution after treatment with adsorbent. With

dilute solutions and by varying the thickness of the compartment from 4 cm to 2, 1 and 0.5 cm,[1] this method gives very accurate results.

If we wish to trace the adsorption isotherm for a wide range of concentration, the accuracy of the compensator plate is unfortunately diminished if the plate has to be turned through such a large angle as to make it difficult to decide whether a given pair of interference bands is of the order 0 or +1 or —1. In this case one of the following methods is to be preferred:

2. One compartment is filled with the original solution, the other with the solution shaken with the adsorbent. The difference of concentration is now comparatively *small*, but, if we are accurate, the same difference of concentration still does not correspond exactly to the same number of scale units for a large range of concentration.

This is illustrated by the data given in the following Table 1, from which it appears that the concentration value μ of each scale unit increases with the absolute concentration, and therefore index of refraction, of the solution as well in the number of scale units.(α) as with the absolute concentration of the solution.

TABLE 1

Solutions of KNO_3

Solutions investigated	Difference of concentration k	Number of scale units α	$\left(\mu = \frac{k}{\alpha}\right) \times 10^4$	Mean concentration	Temperature
H_2O -0 200	0.2000	1579	1.267	0.1	14.98°
0 2000-0 4007	0.2007	1527	1.314	0.3	15.00°
0.4007-0.6006	0.1999	1483	1.348	0.5	15.02°
0.6006-0.8026	0.2020	1465	1.379	0.7	15.20°
0.8026-1.0019	0.1993	1395	1.429	0.9	15.12°
H_2O -0.4007	0.4007	3360	1.192	0.2	15.00°
0.2000-0 6006	0.4006	3235	1.238	0.4	15.05°
0.4007-0.8026	0.4019	3158	1.273	0.6	15.32°
0.6006-1.0019	0.4013	3085	1.301	0.8	15.12°
1.0019-1.4054	0.4035	2957	1.365	1.2	15.27°
1.4054-1.8014	0.3960	2794	1.425	1.6	15.34°

In each separate case the auxiliary c,α curves must be traced separately.

The concentration value of the scale unit (μ) is therefore not a constant but may be expressed generally as

$$\mu = f(\alpha) \cdot f(c) \quad (1)$$

If accurate measurements are to be carried out across a wide range, it is therefore necessary either to determine this concentration-value of the scale unit (μ) in the neighborhood of each c-value or we may proceed according to (3).

For instance, if the initial concentration of the solution is 0.5 moles, we must prepare solutions of 0.4 and 0.519 moles per litre, whereupon the concentration-value, μ, of the scale unit is found by dividing 0.02 with the number of scale units, α, observed with the interferometer. In the case of KNO_3 α is 122.

Thus

$$\mu_{0.5} = \frac{0.02}{122} = 1.64 \cdot 10^{-4}$$

and similarly at the concentration 0.99–1.01

$$\mu_{1\,0} = \frac{0.02}{111} = 1.80 \cdot 10^{-4} \text{ for molar}$$

concentrations, while μ in the vicinity of 0

$$\mu_0 = \frac{0.02}{136} = 1\ 47 \cdot 10^{-4}.$$

3. While $f\ (\alpha)$ is nearly constant for smaller α-values, but a rather complicated function for greater intervals, it was found that $f\ (c)$ is a linear function of c.

Thus for constant α-values

$$\mu = f\ (\alpha)/1 + \gamma c \quad (2)$$

where γ is a constant characteristic for each salt.

This is seen from Fig. 1, which is constructed from the data in Table 1 and the measurements given on this page. This linear relation between μ and c simplifies the method, which was carried out in the following way:

If we, according to (2), once again let α be a variable,

$$\mu = f(\alpha)\ (1 + \gamma c).$$

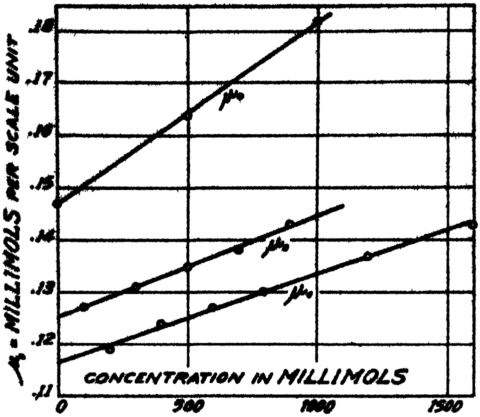

Fig. 1

Multiplying by α we obtain the difference of concentration k between the two solutions A and B as

$$k = \alpha\mu = \alpha f(\alpha)(1 + \gamma c) \qquad (3)$$

For c tending towards 0, i. e., for weak solutions compared with pure water, f (c) is 1 and the equation above mentioned passes into

$$k_0 = \alpha\mu_0 = \alpha f(\alpha) . 1 \qquad (4)$$

or $k_0 = \alpha_0$, if we by α_0 denote the value of αf (α) for c tending towards 0.

Comparing 3 with 4 we have

$$k = k_0 \ (1 + \gamma c). \qquad (5)$$

From this equation 5 we obtain k_0 graphically by plotting k_0 against α_0, thus constructing an auxiliary curve, and γ from the observations related in Table 1. For all alkaline salts γ is nearly 0.00023, but increases for other salts with the atomic weight of the cation. The data for obtaining the auxiliary curve we get, according to (1), by filling the one chamber with water and the other with weak solutions of known concentrations (k_0), and reading off the corresponding α_0 values. In fact, the auxiliary curve of (1) is the same as

with (3), except that the last one only reaches α-values up to 200 s. u.

In order to illustrate the somewhat intricate relations between differences of concentration (k) and angles of the compensator plate, α, we give Fig. 2 where the curve k_0 is the

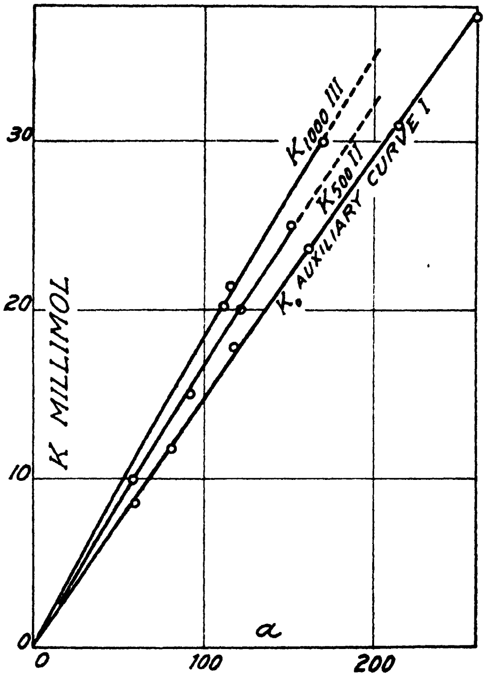

Fig. 2

auxiliary curve (I) obtained in the way just mentioned (weak solutions compared to water). The curve k_{500} is a similar curve, (II) where solutions from 510 to 525 millimoles are compared to a solution with 500 millimoles per litre; and in the curve k_{1000} (III) solutions from 970 to 1000 millimoles are compared with a normal solution (1000 millimoles).

We are able to proceed from any point of the curve I to the corresponding k-values of the curve II or III by means of the relation (5).

$$k_{500} = k_0(1 + \gamma 500), \text{ where } \gamma = 0.00023.$$

TABLE 2
Solutions of KNO_3

Solutions investigated	Differences of concentration millimoles	α
Curve I		
H_2O– 8.8×10^{-3} N. KNO_3	8.8	60
H_2O–11.8×10^{-3} N. KNO_3	11.8	81
H_2O–17.7×10^{-3} N. KNO_3	17.8	118
H_2O–23.7×10^{-3} N. KNO_3	23.7	162
H_2O–31.0×10^{-3} N. KNO_3	31.0	215
H_2O–37.5×10^{-3} N. KNO_3	37.5	261
Curve II		
500×10^{-3} N. 510×10^{-3} N.	10	59
500×10^{-3} N.–525×10^{-3} N.	25	151
510×10^{-3} N.–525×10^{-3} N.	15	92
480×10^{-3} N.–500×10^{-3} N.	20	122
Curve III		
1000×10^{-3} N.–1020.2×10^{-3} N.	20.2	112
999×10^{-3} N.–1020.4×10^{-3} N.	21.4	116
970×10^{-3} N.–1000.4×10^{-3} N.	30	170

The accuracy of this linear relation may be illustrated by following comparison of the differences of concentrations corresponding to 100, 150 and 200 s. u. obtained graphically from curves II and III and calculated from curve I by means of the linear equation.

TABLE 3
KNO_3 $\gamma = 0.00023$

α	k_o curve I	k_{500} curve II		k_{1000} curve III	
		Graph	Calc	Graph	Calc.
s. u	mm	mm	mm	mm	mm
100	14.7	16.4	16.4	18.2	18.1
150	22.0	24.5	24.5	26.9	27.1
200	29.1	32.5	32.4	35.7	35.8

This exact method 2 or 3 is rather tedious if many *c*-points are to be determined. We have therefore investigated the

magnitude of the error, when the adsorbed quantity (y) is calculated with the constant value (μ_0) of μ, in the vicinity of 0 instead according to (3). We have thus found that if c does not exceed 0.1 moles, the error is less than 2%; at 0.2 moles, about 4% and at 1 mole greater than 20%.

As the experimental error in the determination of k can be estimated at about 2%, the above correction may be neglected if we do not exceed concentrations above 0 1 mole.

It remains to discuss the influence upon the measurements of variations of temperature. From the investigations of H. Schmeel,[1] we know that the correction up to 400 scale units is proportional to the number of scale units, and amounts to about 0 4%. This refers to measurements made in the 4 cm chamber. As we have usually worked with the 1 cm chamber, the correction is, of course, only one-fourth of the above, viz., 0 1 percent. Our number of scale units never exceeded 300, and the temperature variation seldom 1°, so that the correction at the utmost would be 0 3 scale units, which is within the limits of the error of observation, and can therefore be neglected. For particulars of the construction and manipulation of the interferometer we refer to the original papers of the constructor[2] and also to the reports of H. Schmeel[3] and O. Arendt.[4]

The agreement between the results of measurements of quantities adsorbed by the interferometrical and other methods is demonstrated by the following experiments:

$RbNO_3$: From a standard solution three portions were taken by means of a precision-pipette.

After evaporating the water in a platinum crucible, the samples were dried to constant weight at 160°. The same operation was carried out with 15 cm of the solution, from which a certain amount had been adsorbed by 0 398 g charcoal.

[1] Dissertation, Freiburg, 1915.

[2] Phys. Zeit., **11**, 1047 (1920) Zeit. Instrumentenkunde, **30**, 321 (1910).

[3] Dissertation, Freiburg (1915), p. 5.

[4] Kolloidchemische Beihefte, **7**, 212 (1915).

Mean value of three analyses of the original solution: 0.1854 moles
Mean value of two analyses after adsorption : 0.1792 moles

Difference 0.0062 moles

Interferometrically determined difference 47 scale units equal to 0.0061[1] $(1 + 0.18 \times 0.212) =$ 0.0063 moles

$Ba(NO_3)_2$: The barium was precipitated as sulphate in the ordinary way.

25 cm of the original solution yielded 0.2910 g $BaSO_4$ = 0.0499 moles
25 cm of the solution after adsorption yielded 0.2486 g $BaSO_4$ = 0.0426 moles

Difference 0.0073 moles

Interferometrically determined difference 166 scale units equal to 0.0076[1] $(1 + 0.046 \times 0.305) =$ 0.0078 moles

3. Preparation and Purification of Adsorbents

As already mentioned, much care was taken to purify the adsorbents. The charcoal employed was always *Carbo sanguinis sicc. pro analysi* from Merck. This charcoal was found to contain small quantities of acids. In order to study the purification, the charcoal was first treated with dilute hydrochloric acid and this acid first roughly washed out. Small portions of the charcoal were then stirred up with hot water and after being shaken the charcoal was separated with the aid of a centrifuge, by means of which the liquid could be removed far better than by filtration. Filtration through ordinary funnels was found to be very unsatisfactory, because it simply resulted in canals forming in the mass, through which the water ran. When the wash-water was free from traces of either acids or chlorine ions, the operation of washing was nevertheless repeated at least three times more with pure conductivity water (of $k = 1 \cdot 10^{-6}$). The various portions were then united, and the whole material repeatedly treated with pure water, separated, pressed on a Büchner funnel and finally dried at 125° and kept in a closed bottle.

As a criterion of purity (which, of course, even in this case, is not absolute), a large portion of the charcoal was re-

[1] This value obtained from the auxiliary curve

quired, when treated with a small quantity concentrated solution of potassium sulphate, to impart to this solution neither an acid nor a chlorine reaction. If the charcoal was to be used as an adsorbent in alcoholic or other organic solutions (see Part III) it was, before treatment with water, repeatedly boiled with the liquids below in the following order: benzene, alcohol, chloroform, alcohol again. Then came the above-mentioned purification with water, and finally, the charcoal was washed with the liquid in which the adsorption was to be carried out, and dried at a low temperature (not above 40°) in vacuo over metallic sodium. If heated above this temperature with traces of adsorbed alcohol, it was found that an oxidation to aldehyde took place which caused errors in the following adsorption measurements.

4. Equivalence of Cations and Anions adsorbed—Nature of Decomposition of Adsorption

If the charcoal is carefully purified in the way above mentioned, equal amounts of cations and anions are adsorbed If this proved not to be the case, as H Lachs and L. Michaelis[1] and other authors have maintained, the solution after adsorption should, by hydrolysis, have either an acid or an alkaline reaction. No such reaction could, however, in any case be discovered either with sensitive indicators (phenolphthalein, litmus) or with the hydrogen electrode.

If the adsorbent is merely washed until the filtrate gives no acid reaction, hydrogen ions could always be detected in the solution after adsorption If the charcoal had as is probably always the case in its technical preparation, been treated with hydrochloric acid and washed until the reaction of chlorine had vanished in the filtrate, and is then treated with an absolutely neutral solution of potassium sulphate, abundant chlorine ions could be detected in the filtrate.

These experiments make it very probable that the so-called decomposition by adsorption (*Adsorptionszersetzung*) is only apparent, the cause being adsorbed impurities (H or

[1] Koll.-Zeit., 9, 275 (1911)

OH ions) which are partially thrown out by the adsorbed solution. If we examine the cases of decomposition by adsorption cited in the literature, this opinion seems to be strongly confirmed.

Thus Fr. Weppen,[1] Esprit,[2] and others found that charcoal, washed with hydrochloric acid, adsorbed the base and set the acid free; whereas R. Warington[3] states that oxides of iron and aluminium precipitated with alkali adsorb the acid.

Moreover, D. F. Tommasi[4] discovered that the blue cupric hydroxide which is obtained from cupric solutions by treatment with alkali, adsorbs more acid than base from solutions of the chlorides of sodium and potassium. On the other hand, peroxide of manganese produced, according to E. Fremy, from $Mn(SO_4)_2$ and water (by which reaction sulphuric acid is set free) is said to absorb the base from a neutral solution of an alkali salt.[5]

A striking fact with regard to these researches is, that those absorbents which are said to adsorb the base and set the acid free are derived from *acid* solutions or have been treated with acids, whereas the adsorbents which appear to adsorb the acid and set the base free are prepared from *alkaline* solutions.

This can hardly be due to chance only, but depends, on the contrary, on the circumstance that the disintegrated constituent which is said to be set free, is in reality retained as traces of acid or base, not washed out, and not detected until thrown out by the addition of the neutral salt solution.[6]

We do not think it necessary to deal with this topic any further, or to cite other experiments of ours in favor of this opinion, because Michaelis, in a later paper,[7] published to-

[1] Liebig's Ann., 55, 241–245 (1845); 59, 354–358 (1846).

[2] Jour. prakt. Chem., 48, 424 (1849).

[3] Ibid., 104, 316–318 (1868).

[4] Comptes rendus, 92, 453–455 (1881).

[5] Van Bemmelen: Comptes rendus, 82, 475–476 (1876).

[6] See the paper by G. C. Schmidt: Zeit. phys. Chem., 74, 689 (1910).

[7] Published May, 1919, and without influence on our, in respect to this topic, already finished work. Cf. also Odén, in Ber. deutsch. bot. Ges., 34, 648 (1916).

gether with P. Rona, has admitted errors in his early method and has found that cation and anion are adsorbed in precisely equivalent amounts.

5. Adsorption of Alkali Nitrates by Charcoal

The measurements are recorded in Tables 5–12, whereas the corresponding curves are graphically traced in Fig. 3.

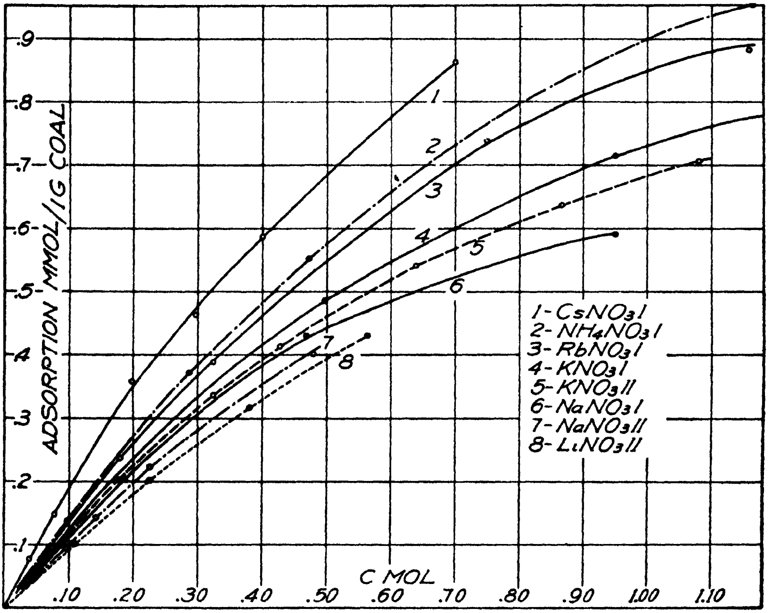

Fig. 3

From the adsorption isotherms with Charcoal I it is seen that the order of adsorption is:

$$Na < K < Rb < NH_4 < Cs$$

and from the isotherms with Charcoal II:

$$Li < Na < K$$

We may thus conclude that within the alkali-group of the periodic system the adsorbed quantity increases with the atomic weight of the cation.

TABLE 4

Salt adsorbed	Mol. weight of cation	K	β
	Adsorbent = charcoal A I		
$CsNO_3$	132.8	0.00440	0.81
$RbNO_3$	85.5	0.00352	0.81
NH_4NO_3	18.0	0.00277	0.86
KNO_3	39.1	0.00185	0.90
$NaNO_3$	23.0	0.00131	0.95
	Adsorbent = Charcoal A II		
KNO_3	39.1	0.00376	0.78
$NaNO_3$	23.0	0.00195	0.86
$LiNO_3$	6.9	0.00178	0.87
	Adsorbent = Charcoal A II		
$Ba(NO_3)_2$	137.4	0.0373	0.45
$Sr(NO_3)_2$	87.6	0.0236	0.50
$Ca(NO_3)_2$	40.1	0.0094	0.63
$Mg(NO_3)_2$	24.3	0.0115	0.58

We also tried to express the adsorbed quantity as function of the remaining concentration by means of the Freundlich formula

$$y = Kc^{\beta}$$

But it is clearly seen from the tables below that, if we calculate the coefficient K and the exponent β from values obtained at low concentrations, the agreement at higher concentrations is not good, and *vice-versa*.

However, if we take a range of concentration 0.1–0.8 moles per litre, it is, of course, possible to determine the two constants of the Freundlich formula. These are recorded in Table 4. It is seen that the coefficient increases from $1.31 . 10^{-3}$ for the sodium salt to $4.4 . 10^{3}$ for the caesium salt, whereas the exponent decreases slightly. It should furthermore be noticed that the curves for the two charcoals have neither the same coefficients nor exponents.

In the following tables:

α_0, is the interferometrical difference in scale units.[1]

k_0, the corresponding concentration.[1]

b, is the concentration of the salt solution (B) before adsorption, expressed in millimoles per 1000 cc.

m, is the amount of charcoal employed expressed in grams.

α, is the interferometrical difference in scale units between the solution before (B) and after adsorption (A) with m grams charcoal per v. (10) cc.

$k_0 = \alpha\mu_0$ is graphically obtained from the auxiliary curve as the k-value corresponding to α, and signifies the difference of concentration at "infinite" dilution or at so low concentrations that all the corrections may be neglected.

$k = k_0\ (1 + \gamma c)$ is thus the difference in concentration (expressed in millimoles per 1000 cc)caused by the adsorption.

$c = b\text{-}k$ is the concentration of the solution after the adsorption.

$y = \dfrac{k \cdot v}{1000 \cdot m}$ is the quantity adsorbed by one gram charcoal from 10 cc solution, expressed in millimoles.

y' (calc) is the value calculated by means of the Freundlich formula

$$y = Kc^{\beta}$$

TABLE 5

Adsorption of KNO_3 by charcoal A I.

Auxiliary curve		$v = 10\text{ cm}^3$; $t = 18.5° - 19.5°$						
k_0	α_0	b	m	α	k_0	k	c	y
8.8	60	987	0.420	171	25.0	30.1	957	0.715
11.8	80	512	0.292	88	13.0	14.4	498	0.495
17.8	118							
23.7	162							
37.5	261							
$\gamma = 0.0023$								

[1] By means of these the auxiliary curve is obtained.

TABLE 6

Adsorption of $NaNO_3$ by charcoal A I

Auxiliary curve		$v = 15$ cm³; $t = 16.5° — 17.5°$							
k_0	α	b	m	α	k_0	k	c	y	y' calc
6.2	42	1001	1.286	317	43.3	52.2	949	0.600	(0.706)
12.5	87	500	1.090	203	28.6	31.6	468	0.434	0.452
13.9	97	200	1.065	97	13.9	14.5	185	0.204	0.188
14.6	103	100	1.157	54	7.8	8.0	92	0.100	0.095
20.5	144	50	1.035	23	3.3	3.3	47	0.048	0.051
25.0	173	25	0.870	6.5	1.0	1.0	24	0.017	0.027
50.0	369								

$\gamma = 0.00020$

The values in the last column are calculated by means of the equation:

$$y' = 0.00131 . c^{0.95}$$

TABLE 7

Adsorption of NH_4NO_3 by charcoal A I

Auxiliary curve		$v = 10$ cm³; $t = 17.°5 — 18.°5$							
k_0	α	b	m	α	k_0	k	c	y	y' calc
10.0	74	1198	0.353	211	27.0	33.7	1164	0.955	(1.205)
17.8	140	500	0.462	180	23.1	25.6	474	0.554	0.556
24.0	186	300	0.301	80	10.5	11.2	289	0.372	0.363
38.5	300	104	0.433	45	5.9	6.0	98	0.138	0.143

$\gamma = 0.00022$

The values in the last column are calculated by means of the equation:

$$y' = 0.00277 . c^{0.85}$$

TABLE 8

Adsorption of $CsNO_3$ with Charcoal A I

Auxiliary curve		$v = 10\ cm^3$; $t = 17.5° — 18.5°$							
k_0	α	b	m	α	k_0	k	c	y	y' calc
2.1	20	730	0.298	214	22.8	26.2	704	0.880	0.900
8.6	78	429	0.505	249	26.4	28.7	400	0.570	0.569
14.4	132	319	0.469	194	20.5	21.6	297	0.460	0.447
28.6	273	214	0.450	137	14.7	15.3	199	0.341	0.323
42.9	416	86	0.509	69	7.5	7.6	78	0.150	0.151
γ = 1.00022		43	0.519	35	4.0	4.0	39	0.077	0.086

The values in the last column are calculated by means of the equation:

$$y' = 0.00445 . c^{0.81}$$

TABLE 9

Adsorption of $RbNO_3$ with charcoal A I

Auxiliary curve		$v = 10\ cm^3$; $t = 18.5° — 19.5°$							
k_0	α	b	m	α	k_0	k	c	y	y' calc
7.9	56	1191	0.358	196	25.5	31.8	1159	0.890	(0.845)
22.5	176	776	0.357	174	22.7	26.4	750	0.740	0.746
44.0	350	339	0.348	97	12.7	13.6	325	0.391	0.389
γ=0.00021		$v = 15\ cm^3$							
		185	0.396	47	6.1	6.3	179	0.241	0.240

The values in the last column are calculated by means of the equation:

$$y' = 0.00352 . c^{0.81}$$

TABLE 10

Adsorption of KNO_3 by charcoal A II

$v = 15\ cm^3$; $t = 16.5° — 17.5°$

b	m	α	k_o	k	c	y	y' calc
1109	0.558	154	21.5	26.4	1083	0.708	(0.839)
889	0.544	138	19.5	23.1	866	0.638	(0.706)
659	0.569	129	18.1	20.6	638	0.543	0.558
444	0.546	97	13.6	14.9	429	0.410	0.411
337	0.576	86	12.1	12.9	324	0.337	0.333
181	0.554	51	7.1	7.3	174	0.204	0.204
117	0.528	35	5.0	5.1	112	0.145	0.146

The values in the last column are calculated by means of the equation: $y = 0.00376 . c^{0.775}$

TABLE 11

Adsorption of $NaNO_3$ by charcoal A II

$v = 10\ cm^3$; $t = 16.5° — 16.7°$

b	m	α	k_o	k	c	y	y' calc
500	0.510	130	18.6	20.4	480	0.400	0.394
234	0.467	70	10.0	10.5	224	0.225	0.205
150	0.525	50	7.1	7.3	143	0.140	0.139
100	0.538	34.5	5.0	5.1	95	0.095	0.098

The values in the last column are calculated by means of the equation: $y = 0.00195 . c^{0.86}$

TABLE 12

Adsorption of $LiNO_3$ by charcoal A II

Auxiliary curve		$v = 10\ cm^3$; $t = 16.5° — 16.8°$							
k_o	α	b	m	α	k_o	k	c	y	y' calc
6.9	41	585	0.477	119	18.4	20.7	564	0.434	0.434
17.1	107	399	0.494	92.5	14.3	15.5	383	0.314	0.314
20.5	129	234	0.487	60	9.5	9.9	224	0.204	0.197
34.3	231	117	0.524	32	5.0	5.1	112	0.098	0.108
41.0	274								

$\gamma = 0.00021$

The values in the last column are calculated by means of the equation: $y = 0.00178 . c^{0.870}$

6. Adsorption of Nitrates of the Alkaline Earths by Charcoal

Similar experiments were carried out with the nitrates of the alkaline earths.

The measurements are recorded in Tables 13–16, and represented graphically in Fig. 4.

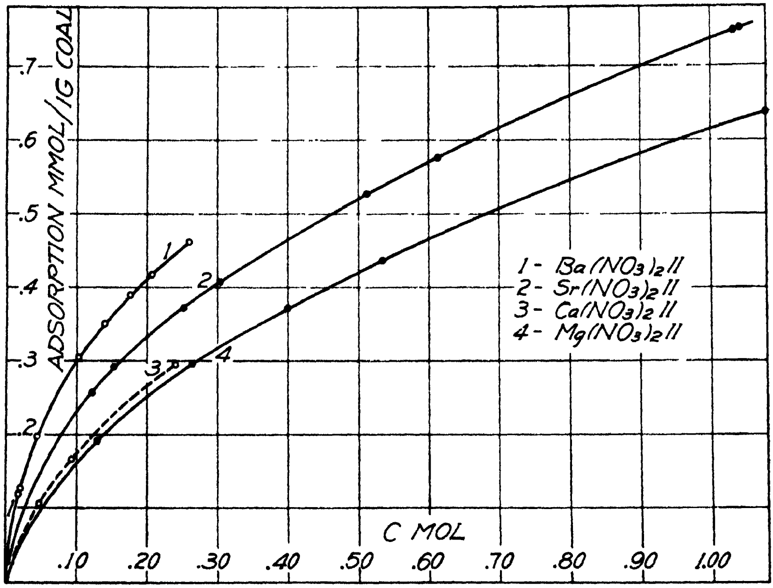

Fig. 4

It is clearly seen that within this group also the adsorbed quantity increases with the atomic weight of the cation, and the coefficient, k, increases at the same time as the exponent, β, decreases slightly (Table 4).

The notation in the following Tables 13–16 is the same as in the measurements with the alkali nitrates.

TABLE 13

Adsorption of $Mg(NO_3)_2$ by charcoal A II

Auxiliary curve		$v = 10$ cm³; $t = 17.9° — 18.0°$							
k_0	a_0	b	m	a	k_0	k	c	y	y' calc
7.0	113	1098	0.351	348	19.5	22.4	1076	0.638	(0.656)
13.9	245	549	0.352	251	14.3	15.4	534	0.436	0.440
27.6	495	412	0.354	218	12.4	13.1	399	0.373	370
42.3	756	275	0.364	180	10.3	10.7	264	0.294	291
$\gamma = 0.00014$		138	0.353	114	6.7	6.8	131	0.193	195

The values in the last column are calculated by means of the equation:

$$y' = 0.0115 . c^{0\ 58}$$

TABLE 14

Adsorption of $Ca(NO_3)_2$ by charcoal A II

Auxiliary curve		$v = 10$ cm³; $t = 18°$							
k_0	a_0	b	m	a	k_0	k	c	y	y' calc
5.0	91	250	0.356	191	10.0	10.5	240	0.295	0.298
12.9	253	100	0.353	107	5.7	5.8	94	0.165	164
17.7	340	50	0.358	71	3.8	3.8	46	0.107	105
25.2	498	5	0.337	13	0.7	0.7	4	0.021	023
50.0	983								
$\gamma = 0.00021$									

The values in the last column are calculated by means of the equation

$$y' = 0.00944 . c^{0\ 63}$$

TABLE 15

Adsorption of $Sr(NO_3)_2$ by charcoal A II

Auxiliary curve		$v = 10$ cm³; $t = 17.8° — 18.5°$							
k_0	α	b	m	α	k_0	k	c	y	y' calc
4.0	78	1066	0.334	413	20.0	25.1	1041	0.752	0.753
8.1	156	639	0.370	371	18.3	21.1	618	0.570	581
10.7	210	322	0.346	270	13.5	14.5	307	0.405	408
16.1	334	160	0.358	203	10.2	10.6	149	0.295	285
32.2	672	1064	0.389	479	23.3	29.1	1035	0.748	752
$\gamma = 0.00024$		532	0.358	340	16.8	18.9	513	0.527	528
		266	0.345	241	12.1	12.8	253	0.371	371
		133	0.411	205	10.3	10.6	122	0.257	254

The values in the last column are calculated by means of the equation

$$y' = 0.0236 . c^{0.50}$$

TABLE 16

Adsorption of $Ba(NO_3)_2$ by charcoal A II

Auxiliary curve		$= 10$ cm³; $t = 17.4° — 18.0°$							
k_0	α	b	m	α	k_0	k	c	y	y' calc
2.5	54	286	0.426	407	18.1	19.7	267	0.463	0.463
5.0	107	225	0.400	346	15.5	16.6	209	0.415	413
7.5	159	193	0.410	339	15.2	16.1	177	0.390	384
11.7	270	153	0.370	275	12.3	12.9	140	0.350	347
23.0	514	113	0.319	209	9.5	9.8	103	0.304	299
25.0	570	50	0.391	166	7.6	7.8	42	0.198	200
$\gamma = 0.00031$		25	0.298	78	3.7	3.7	21	0.125	(147)
		23	0.360	92	4.2	4.2	19	0.118	(141)

The values in the last column are calculated by means of the equation

$$y' = 0.373 . c^{0.45}$$

Upsala, 1920

THE APPARENT IRREVERSIBILITY OF THE CALOMEL ELECTRODE

BY A. W. LAUBENGAYER

Paschen[1] has pointed out that a mercury anode polarizes much more strongly in hydrochloric acid than in sulphuric acid. He attributes this difference to the formation of a coherent film of calomel. Since there was no obvious theoretical reason why a mercury anode should behave differently in the two solutions and since the difference of behavior, if real, might have a distinct bearing on the behavior of the calomel electrode, Professor Bancroft suggested that I make some voltage-current runs under various conditions as part of my senior thesis. Preliminary qualitative experiments with a mercury anode in hydrochloric acid solution showed that the anode became coated with a black film having a high apparent resistance. In the quantitative runs, a piece of 7 mm glass tubing was bent round at the bottom and blown so as to form a cup two centimeters in diameter which was filled with mercury and served as the anode. The cathode was a small piece of platinum foil. In the runs with a platinum anode, the latter resembled the platinum cathode but was bent horizontally so that it could be covered with the mercury salt. The electrodes were placed in a glass beaker. A Leeds and Northrup student potentiometer set was used to measure the voltage drop while the current was measured with a very sensitive galvanometer for small values and on a milliammeter for higher values.

The following systems were studied:

Hg (anode), M/1 HCl, Pt (cathode).
Hg (anode), Hg_2Cl_2, M/1 HCl, Pt (cathode).
Hg (anode), Hg_2Cl_2, M/1 KCl, Pt (cathode).
Pt (anode), Hg_2Cl_2, M/1 HCl, Pt (cathode).
Hg (anode), M/2 H_2SO_4, Pt (cathode).
Hg (anode), Hg_2SO_4, M/2 H_2SO_4, Pt (cathode).
Pt (anode), Hg_2SO_4, M/2 H_2SO_4, Pt (cathode).

[1] Wied. Ann., 39, 61 (1890).

The mercury was the pure redistilled product as obtained from the Department of Physics. The calomel was prepared by precipitation from dilute mercurous nitrate solution by pure hydrochloric acid. The mercurous sulphate was made by the electrolytic method as described by Clark.[1] Normal solutions of hydrochloric acid, sulphuric acid, and potassium chloride were made up in sufficient quantities so that all runs were made with the same solutions. The results for sulphuric acid are shown graphically in Fig. 1 and

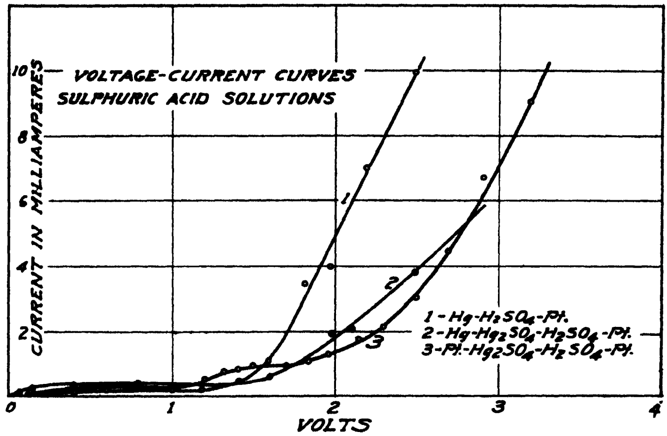

Fig. 1

for the chlorides in Fig. 2, the voltage drop being measured along the abscissas and the current along the ordinates.

The curves in Fig. 1 are quite normal, the break coming at about the same place with the two mercury anodes and the curve rising less rapidly with the one for the solution containing mercurous sulphate, because of the increased resistance. Owing to lack of time no special study was made of the system with mercurous sulphate and platinum anode, as the important point for this investigation was merely the relative position of this curve as compared to the corresponding curve in the chloride solutions. In Fig. 2 we get a sharp

[1] The Determination of Hydrogen Ions, 157 (1920).

break for the platinum anode; but the other three are quite abnormal. With a potential drop of six volts the current is less than one milliampere as against ten milliamperes for two volts with a platinum anode, and as against four and ten milliamperes with two and a half volts for a mercury anode in a sulphate solution. A high resistance film is evidently formed on the mercury in all the chloride solutions. This is brought out more clearly in Fig. 3 which shows the behavior

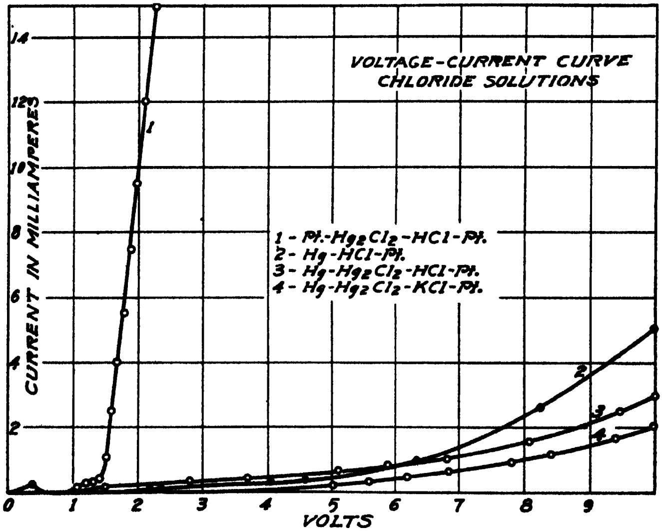

Fig. 2

at lower voltages. The ordinates are galvanometer readings which can be converted into milliamperes approximately by multiplying by 0.016. With a mercury anode in hydrochloric acid and no mercurous chloride, a current of about 0.2 milliamperes can pass before the film forms. When mercurous chloride is present in excess, the film forms at a lower current and lower voltage; but appears not to have quite so much resistance. There are a number of points in connection with these experiments which call for further study; but the only

one that can be settled now is the composition of the high-resistance film.

With mercury as anode in hydrochloric acid a silvery gray film formed at a low voltage which became darker and finally quite black as the voltage was increased. The film was removed carefully and examined under the microscope. It appeared to be composed of finely divided drops of mercury and some whitish, transparent, crystalline material. When this crystalline substance was treated with dilute ammonia

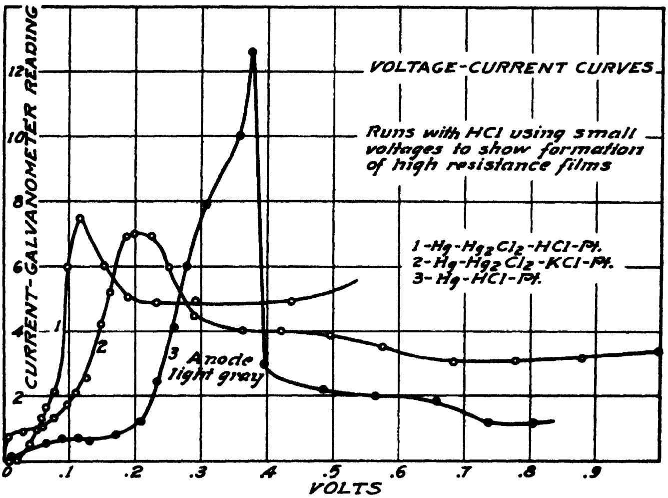

Fig. 3

it turned black, thus giving the test for calomel. Calomel was prepared electrolytically as recommended by Clark.[1] Under the microscope it presented practically the same appearance as the product obtained by anodic polarization.

The experiments show that the apparent irreversibility of the calomel electrode is not real; but is due to the formation on the surface of the mercury anode of a strongly adsorbed film of mercurous chloride, which offers a high resistance to the passage of the current. If this is scraped off as fast

[1] The Determination of Hydrogen Ions, 135 (1920).

as formed, it becomes a simple matter to prepare calomel electrolytically[1] at a relatively low voltage. We do not know why mercurous chloride should behave so differently from mercurous sulphate in regard to forming a high resistance film. I am indebted to Professor Chamot for aid in making the microscopic analysis and to Professor Briggs for suggestions in regard to many details of the work.

Cornell University

[1] Lipscomb and Hulett: Jour. Am. Chem. Soc., **38**, 21 (1916).

NEW BOOKS

Plantation Rubber and the Testing of Rubber. *By G. Stafford Whitby. 22 × 14 cm; pp. vi + 559. New York: Longmans, Green and Co., 1920. Price: $9.00.*—In 1906 the plantation rubber was less than one percent of the total annual crop. To-day it is about ninety percent The increased production of raw rubber has been absorbed chiefly by the rubber manufacturing industry in the United States which took over nearly six times as much raw rubber in 1917 as in 1910. The author has really given us two books in one cover, the first on the preparation of plantation rubber and the second on the testing of rubber.

The plantation rubber trees are practically entirely *Hevea brasiliensis.* Plantations in the Malay peninsula and Sumatra planted with six-months-old stumps show after four years perhaps sixty percent of the trees with a girth of eighteen inches or more at a height of twenty-two inches from the ground, which is the standard size for beginning tapping In Ceylon and Java the rate of growth is less. The present tendency is away from the V-system of tapping and toward a single cut on one-third or one-quarter of the circumference. There is still no agreement as to the physiological significance of the latex, p. 23. There is an admirable chapter on the coagulation of latex, pp 31–75 Beadle and Stevens claim that the resin does not exist in the latex detached from the caoutchouc, p 81, while DeVries claims that if latex is coagulated in two fractions, two-thirds of the resin goes into the first fraction These apparently contradictory results may be due to the different way in which the two sets of experiments were made. The author apparently endorses van Rossem's view on tackiness, p 106, that depolymerization or disaggregation is the fundamental cause of tackiness, but under ordinary circumstances the presence of oxygen is essential to tackiness because depolymerization would not normally take place in the absence of oxygen. It is now recognized that the protein content of rubber may have a marked effect on the rate of vulcanization, p. 120.

Practically all the plantation rubber is coagulated by acetic acid, p. 144, partly because a slight excess of acetic acid has very little harmful effect on the properties of the rubber, which is not true in the case of the mineral acids, p 147. "Practically all the rubber is prepared in one of two forms: crêpe and sheet. In the preparation of crêpe the wet coagulum is broken up (masticated) and washed on mills over the rolls of which a stream of water is running, and is then rolled out thinner into crêpe ribbons. In the preparation of sheet, the coagulum, which must have been made of a suitable slab shape, is rolled out between smooth rolls moving in opposite directions at equal speeds. The effect of this rolling is to squeeze out the (readily putrescible) serum and give a sheet of wet rubber, which, under suitable drying conditions, will dry without the occurrence of putrefaction. The drying is usually done in an atmosphere of warm wood smoke. In the case of crêpe the (putrescible) soluble, serum substances are removed with considerable completeness by the mastication, washing and rolling. The wet crêpe is most usually allowed to dry in the air. Sheet does not undergo any mastication." In Malay and Sumatra crêpe is

usually air-dried, p. 163; but in Ceylon artificial drying is employed frequently, using vacuum or hot air driers. "In the preparation of sheet, the wet coagulum is not, as in the preparation of crêpe, broken up on mills, but, having been formed in slabs of suitable dimensions, is merely rolled out, by being passed between rolls moving at even speeds in opposite directions. Although the rolling has the effect of removing most of the serum from the coagulum, it does not remove the serum as completely as it is removed in the preparation of crêpe. Hence, sheet has a tendency, not encountered in crêpe, to become mouldy on the surface. To overcome this tendency, and at the same time to regularize and hasten the drying of wet sheet, it is usual to dry it in wood smoke."

"It is generally recognized that samples of crêpe vulcanize more slowly than comparable samples of sheet. The milling to which the wet coagulum is subjected in the preparation of crêpe has the effect of removing the serum more completely than it is removed in the preparation of sheet; and to this more complete removal is to be ascribed the slower rate of cure of crêpe as compared with sheet. The milling in question appears to be without appreciable influence on any of the vulcanizing properties except the rate of cure."

"Inorganic substances, such as, conspicuously, litharge, magnesia and lime, the presence of which accelerates vulcanization, have long been known, and have always been widely used in the manufacture of rubber goods. Within recent years many organic substances which accelerate vulcanization have been brought forward, and are now the subject of eager industrial investigation The existence of organic accelerators was first signalized in 1912 by Hofmann and Gottlob on behalf of the Bayer Company. Piperidine, its homologues and derivatives were the compounds the use of which was proposed. It was stated that a mix of 100 parts of Para rubber and 10 parts of sulphur, which required ordinarily more than one hour for its vulcanization at 53 lb. steam pressure, could be vulcanized perfectly in fifteen minutes if 0 5 parts of piperidine were added.

"The impulse to the discovery of the accelerating action of piperidine on vulcanization came from the difficulty which the vulcanization of synthetic caoutchouc offered in the absence of a catalyst. Since 1912 a very large number of organic substances have been found capable of accelerating vulcanization. Indeed, Bayer and Co. have claimed all ammonia derivatives of a basic reaction and all nitrogenous organic bases which possess a dissociation constant greater than 1×10^{-8}."

"Prior to the advent of plantation rubber the most important rubber sort available to the rubber manufacturing industry was the rubber, prepared from wild trees of *Hevea brasiliensis* in the region of the Amazons, known as Fine Hard Para. In the preparation of Fine Hard Para, undiluted latex, in very thin layers, obtained by dipping a paddle into the latex or by pouring latex over a paddle or over a part of a pole, is subjected to the action of smoke. Layers are superimposed until a large mass is built up.

"The experience of the rubber manufacturing industry with Fine Hard Para has been a long one; and, naturally, this grade of rubber has in some measure assumed the position of a standard in regard to discussions concerning the quality of plantation rubber. It is generally conceded that the chief defect of plantation rubber now put on the market, when considered as a whole and compared

with Fine Hard Para similarly considered, is its lack of uniformity—perhaps particularly in respect of rate of cure."

The second half of the volume is devoted to the testing of rubber and there is given an account of investigations made by physicists into the physical properties of rubber, p. ix. "These investigations, although for a large part comparatively remote in date and without immediate practical bearing, have been described in considerable detail, because of their frequent suggestiveness, and of the circumstance that hitherto they have been almost entirely overlooked by rubber technologists. The (generally excusable) failure in these investigations to appreciate how wide is the variety of mixtures which may be described as 'rubber,' and how greatly the physical properties of 'rubber' are susceptible of variation as a result of variation in the character of the mixtures used and in the conditions of vulcanization (most of the investigators describe their material merely as 'rubber'), detracts a little from the direct value of these investigations, but hardly from their suggestiveness It would seem desirable that some at least of the studies which have been made by physicists on the properties of rubber should be extended over a wider range of physical effects, and with reference to systematic variations in the character of the rubber 'compounds' and in the conditions of vulcanization It would not be unfair to say that, in proportion to the importance of rubber as a constructional material in modern life, and considering the uniqueness of its properties, the physical properties of rubber have not yet received their due amount of exact experimental study "

The titles of the chapters are· the rubber tree and the extraction of latex; latex and its coagulation; the resin; the protein; collection of latex and coagulation in the factory; crêpe; sheet; maturation variation; the stress-strain relations of rubber and the modulus of elasticity; technique of tensile tests; technique of vulcanization testing; progressive changes on vulcanization; comparison of raw rubber samples, stability of state of cure, technical mixes; viscosity determinations; cycles of extension and retraction—hysteresis; elastic aftereffect; relation of the thermal, optical, and electrical to the mechanical behavior of rubber, Poisson's ratio.

This is a valuable book and will prove valuable both for what it tells and for what it suggests. *Wilder D. Bancroft*

Chemistry of Pulp and Paper Making. *By Edwin Sutermeister. 22 × 15 cm; pp. vii + 479. New York: John Wiley and Sons, 1920. Price: $6.00.*— The subject is presented under the following headings: cellulose; fibrous raw materials; rags, esparto, straw, bamboo; the soda process; the sulphate process; the sulphite process; ground wood or mechanical pulp; bleaching; sizing; loading and filling materials; coloring; coated papers; water; testing wood pulps; paper testing; printing.

Under fibrous materials, p. 44, it is pointed out that seven states in the corn belt produce annually about eighty million tons of corn stalks of which the greater part is practically a waste, and that bagasse, the crushed stalks of the sugar cane, is produced in large quantities in the sugar industry and is generally burned as fuel, though its value for this purpose is comparatively low because of the amount of water in it. "Both of these materials can be re-

duced to a pulp quite easily by the soda process and the pulp will bleach to a good white color with less than ten percent of bleach. The ash in the stalks is considerably lower than that in straw and contains much less silica, so that its effect on the recovery process is very slight. The pulp from both raw materials consists of long thick-walled fibers mixed with shorter fibers of similar structure and cells of various shapes and sizes. These include serrated cells of comparatively large size, long thick cells with rounded ends and many pith cells which are so thin-walled that nearly all become flattened during the reduction process. These pith cells are much larger than those from straw and are therefore much more difficult to remove by washing. They impart to the paper made from this fiber a hardness and rattle which are undesirable in many products, and as their separation from the rest of the fiber has proved very difficult the presence of pith has proved one of the chief stumbling blocks in the way of using either bagasse or corn stalks."

While bamboo is not of immediate interest in this country (p. 86), it seems destined to hold an increasingly important place as a source of fiber because of the rapidity of its growth and the high quality of the paper which can be made from it. Raitt estimates that with poor growth the annual yield of stems, air dry, would be 11 tons per acre while it might run to 44 tons with luxuriant growth. He states that in Lower Burma alone there is an area of about 20,000 square miles easily available.

In the chapter on the sulphate process, p. 141, the author says: "The sulphate process is similar to the soda process in that the cooking liquor is alkaline, but it differs from it by replacing the alkali lost with sodium sulphate instead of soda ash. In rare cases both are used but the sulphate is always in the greater amount and it is from the use of this material that the process gets its name. Actually it is a misnomer, and it would be better to call it the sulphide process because of the important part played by sodium sulphide in the cooking liquor. This sulphide is derived from the sulphate by reduction in the recovery of the alkali and it is this feature which introduces the greatest deviation from the soda process. There is more or less confusion in the use of the terms 'sulphate' and 'kraft' as applied to the process and products. Sulphate may be considered as a general term applying to any cooking process in which the loss of alkali is made up by adding sodium sulphate, while kraft is that subdivision of the sulphate process in which the pulp is intentionally under cooked in order to produce very strong stock. The products of the sulphate process vary according to the cooking conditions from the dark brown, unbleachable kraft fiber to a soft, easy bleaching, stock. The latter may be used in making white papers, where it gives a soft, pliable sheet in comparison with the harder and more rattly paper from sulphite. The principal use of the sulphate process, however, is in the preparation of kraft stock.

"The sulphate process has two chief advantages over the sulphite process: the chemicals used can be recovered and the wood used may be of highly resinous nature. It is this second fact which gives the process its widest application. As compared with the soda process it gives somewhat higher yields and employs a cheaper source of alkali. Its one disadvantage lies in the extremely disagreeable odors due to the organic sulphur compounds formed during cooking and recovery. This has been found serious enough to limit its use to sparsely inhabited localities."

There is an unexpected statement on p. 191 in regard to the sulphite process. "Overcooking may also result from the decomposition of the liquor with formation of free sulphur according to the reaction

$$3SO_2 = 2SO_3 + S.$$

The sulphur acts catalytically producing further decomposition of the calcium bisulphite, and the sulphuric acid combines with the lime as $CaSO_4$ so that not enough base is left to combine with the sulphonic acids, which polymerize and eventually the fiber is attacked and darkened. Selenium in the cooking liquid will also act catalytically and with far greater power than free sulphur. Torgerson and Bay have proved that it is not the selenium directly, but the simultaneous presence of dust that causes the trouble. This dust acts as an energetic contact substance, promoting catalytic action of selenium."

The paragraphs on the production of alcohol are interesting, p. 205, though the costs seem much too low. "The preparation of alcohol from waste lyes has probably attracted more attention than any other method of utilization and a number of commercial plants are already in successful operation. The two principal processes now in use are the Swedish, which is a combination of the Wallin and Ekström processes, and the Norwegian or Landmark method. The principle of all processes is the fermentation of the sugars present followed by the distillation of the alcohol formed, and one of the principal difficulties encountered has been due to the poisoning of the yeast by traces of sulphur dioxide. The Swedish process uses a tempered yeast which is capable of resisting this action The liquor is first neutralized by calcium carbonate and the last traces of acidity by calcium hydroxide, it is then cooled, settled and run to the fermentation vats where the yeast is added It is fermented at 27°C for four or five days and then distilled. The raw alcohol contains 92 to 93 percent of ethyl alcohol, 3 to 4 percent methyl alcohol and small amounts of cymol, acetone and aldehyde The yield of 100 percent alcohol by this process is said to be 74 liters per ton of dry sulphite, and the cost about 12 cents per U. S. gallon 180 proof.

"In the Norwegian process the fermentation is aided by a nutrient and easily fermentable medium prepared from milk or whey. To the milk an equal volume of sulphite liquor is added and a small amount of muriatic acid and the precipitated ligno-casein filtered off. The filtrate is then added to the waste liquor and the mixture evaporated to a concentration of about 15 percent. It is next neutralized by powdered limestone, cooled to 27°C and the yeast added, in this case ordinary brewers' yeast has proved entirely satisfactory After four or five days' fermentation it is ready to be distilled. The yield by this process is claimed to be 91 2 liters of 100 percent alcohol per ton of dry sulphite, and the cost about 9 cents per U. S. gallon 180 proof."

Some colloid chemist should certainly study the whole problem of sizing, p. 257. "For some purposes papers are required to be porous and absorbent, in order to allow the passage of fluids, as in filter paper, or their rapid absorption as in blotting paper, but for most applications, which imply the use of ink of some kind, it is desirable that they be more or less non-absorbent This is particularly essential in the case of writing papers which come in contact with very fluid inks, and in papers which are to be used for coating, and it is even considered of importance in printing papers though the nature of printing inks

is such that good letter-press work can be done on an unsized or water-leaf paper. Since the absorbent power of paper depends on the capillary action of the fiber surfaces and on the spaces within and between the fibers, it is necessary, in order to make the paper non-absorbent, to coat the fibers with some substance which will offer resistance to the passage of ink. This object is accomplished by various methods of sizing.

"The degree of sizing and the nature of the agents employed depend upon the use to which the paper is to be put. For newspaper, on which the ink must dry very rapidly and almost wholly by absorption, the sizing must be slight so that capillary action may not be prevented; for book papers the sizing is usually harder than for news, not because the inks used are more easily absorbed, but because the sizing makes the paper more satisfactory for general service; for lithograph papers the sizing must be still harder because the paper becomes moistened during printing, while for writing papers on which very fluid inks are used the sizing must be particularly hard so that the ink may not spread and the lines become blurred. In the days of hand-made papers the sheets were sized by dipping them into a tub of gelatine solution and the process was known either as tub or animal sizing from the nature of this operation. A modified form of this process is still employed and as it consists essentially of the deposition of a layer of the sizing material on the surface of the paper it might well be spoken of as surface sizing. This method of sizing is too slow and expensive for the great bulk of modern printing papers and for such other processes have been devised. Most of these depend upon the precipitation on the fibers of some material which on drying renders the sheet either repellent or resistant to moisture and as this operation generally takes place in the beating engine it is usually called engine sizing."

"The drying of animal sized papers is a matter of particular importance since the quality of the product depends largely on this operation. It is desirable to dry slowly, without agitation and at a temperature below that required to liquefy the jelly so that the problem is really that of drying a jelly rather than a solution. Loft drying is the best but the slowest and most expensive, the festoon arrangement used in drying coated papers gives fair results but is not perfect, while if the paper is dried on a steam cylinder the glue has little sizing power since individual fibers only are coated and the interstices are vacant. Papers dried on the skeleton drums are subjected to so much vibration from the fans that the surface tends to crack and the product is therefore inferior to loft dried paper. If, after drying, the sizing is found to be defective it may sometimes be improved by wetting and again drying. The temperature of drying depends in part on the atmospheric humidity. If this is low the drying takes place rapidly and a correspondingly low temperature may be employed but if the humidity is high the temperature must be raised to permit evaporation to take place. The upper limit is set by the liquefaction of the sizing, which in general may be said to take place at lower temperatures with the poorer grades of glue than it does with gelatines.

"Surface sizing makes paper stronger and firmer and gives a better surface for writing than does engine sizing. Its effect is reduced by the subsequent operations of calendering, rolling or plate glazing which explains the fact that papers with a rough surface are more easily hard sized than those which are

highly glazed. The operation of surface sizing with glue, while apparently a simple one, is in reality one of the most difficult and uncertain of all those carried out by the paper maker, since the gelatine is influenced to so great an extent by atmospheric conditions and its absorption is so dependent on the physical and chemical conditions of the paper employed."

The author says, p. 311, that "paper colored with Prussian blue has the peculiarity that exposure to sunlight decolorizes it partially; the full shade is developed again, however, when the paper is kept in the dark in contact with the oxygen of the air." In "Application of Dyestuffs," p. 523, Matthews says that Prussian blue on wool is fast to light, washing, and exposure. In "Materials for Permanent Painting," p. 152, Toch says that "Prussian blue is a good drier and is perfectly permanent when used alone, provided it is unglazed or is painted over a solid ground. When Prussian blue or any of its analogues is mixed with white lead the rich sky-blue or greenish tint which will result bleaches over night to a sickly green; but the original color comes back on exposure to the light for an hour." Somebody should reconcile these apparent discrepancies.

It is sad, but perhaps to be expected, that the mercerization of cotton should be attributed, p. 20, to the formation of a definite chemical compound. This is only one of a number of cases where the author harks back too far for his authority. The quotations that have been given show that the book is of distinct interest to a much wider circle than only those interested directly in the manufacture of paper, though of course it was primarily for these that the book was written. *Wilder D. Bancroft*

The Manufacture of Sugar from the Cane and Beet. *By T. H. P. Heriot. 22 × 14 cm; pp. xi + 426. New York: Longmans, Green and Co., 1920. Price: $8.50.*—In the preface the author says: "It has often been stated that the sugar producer can only be trained in the factory, theoretical knowledge being of little value. The aim of the present work is to show that successful practice is becoming more and more dependent on scientific principles, which can be studied more effectively outside the factory than inside."

The subject is presented under the general headings: the raw materials; extraction of juice from the cane; extraction of sugar from the beet; composition of cane and beet juices; treatment of cane and beet juices; evaporation of water from the juice; crystallization; special methods of extracting sugar from molasses; by-products; refinery of cane and beet sugars.

The distribution of the constituents in the cane-stem is outlined on p. 136. "As the cane stem ripens from below upwards, the juices extracted from the upper and lower joints of the same stem, differ in composition. The uppermost, green joints contain scarcely any sugar, but some starch; the latter being transformed into fiber during the growth of these joints. A little lower down are joints bearing young leaves, and in which sugar is being stored, chiefly glucose and fructose; the starch having been consumed in the formation of fibre. Still lower down, are joints bearing fully developed leaves, in which starch sugar-production is very active. Here, sucrose begins to accumulate in the stem, while the reducing sugars (also formed) ascend to the upper joints and leaves, and are there transformed into fibre.

"Hence, as each joint approaches maturity, it contains an increasing percentage of sucrose, and a decreasing percentage of reducing sugars. Still lower on the stem, are the fully mature joints whose leaves have withered. This portion receives sucrose from the higher joints, in exchange for reducing sugars, which continue to ascend towards the growing joints; so that the reducing sugars disappear almost completely, and the percentage of sucrose reaches its maximum, and does not increase further during the ripening of the upper joints of the stem. Finally, in those joints to which the roots are attached, sucrose is inverted, in order to supply reducing sugars to the growing roots; these sugars being transformed into fibre or root-structure. The sweetest joints of the stem are therefore those just above the ground level.

"The juice extracted from a single cane-stem must therefore be a mixture of the juices contained in its numerous joints, which explains the invariable presence of reducing sugars. The organic acids, nitrogen compounds, gums, and mineral matters are more abundant in the uppermost joints; gradually diminishing to the minimum percentages in the fully ripe, lower joints. The leaves contain more mineral matter than any other portion of the plant. In overripe cane, a part of the sucrose becomes inverted in the lower joints, and the maximum sucrose-content is then found towards the middle of the stem, diminishing downwards toward the ground, while the percentage of reducing sugars simultaneously increases."

The sugar producers make use of foaming to remove some impurities, p. 176. "The juice is limed, heated to boiling-point in the juice-heater and subsided in settling tanks. The hot, clear juice is decanted from the sediment and boiled briskly in the eliminator pan (where it may be treated with phosphoric acid). Any suspended impurities (which have not subsided in the settling tanks) rise into the foam of boiling juice, this foam being 'brushed' over the top of the eliminator pan into a gutter surrounding it. This operation is essential in the manufacture of Demerara yellow sugar."

Apparently calcium sulphite adsorbs the non-sugars, p. 185, and it is also stated, p. 185, that potassium sulphite is acid to phenolphthalein. This latter seems improbable and the first statement should be checked independently. It seems surprising that the process of double carbonation, p. 233, should not have been developed earlier. "In the process described above, certain of the precipitated non-sugars and coloring matters re-dissolve during carbonation, as soon as the alkalinity of the juice falls below a certain limit. If carbonation be stopped before this limit is reached, the filtered juice remains excessively alkaline, and the subsequent crystallization during boiling in the vacuum pan is rendered difficult.

"Both objections are avoided by conducting the carbonation in two stages, hence the name "double-carbonation." The first stage precipitates the bulk of the lime, leaving the juice sufficiently alkaline (0.07 to 0.10% CaO), to prevent any of the precipitated non-sugars from re-dissolving, and this precipitate is at once removed by filtration. The clear-filtered juice is again carbonated, in order to neutralize the remaining alkalinity, causing a second precipitation of calcium carbonate which is removed by a second filtration, yielding transparent neutral juice of a light color."

The phenomena of crystallization on cooling are interesting, p. 288.

"When a crystallized syrup-massecuite is allowed to cool *in tanks*, or *cisterns*, the rate of cooling is greater at the surface and sides than towards the center; consequently, a large quantity of false-grain is formed, and the true-grain tends to subside, leaving a layer of super-saturated mother-liquor at the surface. After cooling, the true-grain becomes cemented together by a glutinous mixture of mother-liquor and false grain, forming a hard mass, which must be broken up in a special machine (pug-mill) before it can be treated in the centrifugals. Moreover, the false-grain is deposited in the interstices between the true-grain, thus retarding the escape of the mother liquor from the centrifugal basket. A large part of this false-grain escapes through the centrifugal liners, along with the molasses."

"It is important to note that a given massecuite yields the same weights of sugar crystals when cooled at rest as when cooled to the same temperature in motion, but the practical results are very different. For, as explained above, cooling at rest produces a large quantity of false-grain, much of which is lost during centrifugal treatment; whereas, cooling in motion causes continued growth of the true-grain, and the whole of the crystallized sucrose is recovered in the centrifugals in the form of coarse crystals, of high purity.

The use of yeast as food is discussed on p. 377. "The great scarcity of nitrogenous fodder in Germany during the war, led to the synthetical production of fodder by the following processes. The 'fixation' of atmospheric nitrogen had been adopted as a source of nitrates for explosives, and this process also produced considerable quantities of ammonium salts. This ammonia was converted into protein (organic nitrogen compounds) through the agency of yeast, in other words, ammonia salts can feed yeast, and yeast can feed cattle, horses, and human beings. The carbon food for the yeast was supplied by sugar in beet-molasses, and a special variety of yeast was selected, producing no alcohol and multiplying twice as rapidly as distillery-yeasts. The yeast was grown in diluted molasses in fermenting-vats as large as swimming-baths; 100 parts of sucrose in the molasses yielding 76 parts by weight of dried-yeast, containing 50% of protein (derived from the added ammonium salts, or originally taken from the atmosphere)...

"For use as human food, the pressed-yeast is mixed with starchy materials and baked; or is digested with a concentrated sugar solution, which is then concentrated to a thick syrup resembling malt-extract, and containing about 20% of protein. It is of interest to note that yeast can consume nitrogen in the form of urea, as well as in the form of ammonium salts. Hence the nitrogen excreted in the urine of cattle can be re-converted into protein by the agency of yeast, and used as food again; thus producing a continuous cycle, namely, protein to urea in the animal body, and urea to protein in the yeast-cells."

In the last paragraph, p. 411, the author remarks appropriately: "In concluding this brief study of the sugar factory and refinery, attention may be drawn to the fact that the remarkable technical progress made within the past century has not been effected by the so-called practical man, or sugar producer, but by a comparatively small number of men who built the theoretical foundations upon which modern practice stands. Many centuries of practical experience failed to improve the primitive methods of cane-sugar manufacture. Theory evolved a new plant (the sugar-beet); discovered and perfected a new method

of extracting the sugar; and within 85 years enabled Germany to produce over a million tons of beet-sugar per annum!" *Wilder D. Bancroft*

Soil Alkali. *By F. S. Harris. 20 × 14 cm; pp. xvi + 258. New York: John Wiley and Sons, Inc., 1920. Price: $2.50.*—In the preface the author says: "There are hundreds of millions of acres of land in the world that are at present not used for agriculture but which might become productive if the alkali could be eliminated. The need for more land to supply food for the world's increasing population is making a very insistent demand that some of these alkali lands be made available. The response to this demand will depend on a better understanding of the nature of alkali and methods of reclaiming land impregnated with it. This accounts for the new interest that is being shown in the study of soil alkali."

As applied to the soil, alkali refers to any soluble salts that make the soil solution sufficiently concentrated to injure plants. This includes the chlorides, sulphates, carbonates, and nitrates of sodium, potassium and magnesium, and the chloride and nitrate of calcium. The sulphate and carbonate of calcium are not sufficiently soluble to be injurious to crops. Most of the alkalies are in reality neutral salts.

"Whenever the word 'alkali' is mentioned there immediately arises in the minds of some people a vision of desolation. They may picture to themselves a barren tract of land devoid of vegetation and covered with a blanket of white salt mixed with earth; or they may fancy that they see worthless wastes of what had been fertile fields. They imagine beautiful trees being reduced to stumps and fence posts and remnants of farm buildings gradually being eaten away by a slowly advancing white cover, which will eventually reduce the entire landscape to a gray barrenness. Probably each of these pictures has a prototype in some local section. Alkali does prevent the cultivation of vast areas of land, and it has caused the abandonment of many fertile fields; but to give up all effort when alkali makes its appearance would be like abandoning a farm just because some crop became infested with a pest."

"It has been estimated that about 13 percent of the irrigated land of the United States contains sufficient alkali to be harmful. This means that there are over nine million acres of land under present canal systems that are affected with alkali. There are many more million acres of alkali land in the United States that do not lie under irrigation systems. Similar figures might also be given for other countries of this continent and for all of the other continents. The alkali problem is one of no mean importance to farmers, nor to any who are interested in the world's food-supply."

In handling alkali land the source of the salt should be known. "In one region an irrigation canal passed through a shale hill that was very high in soluble salts. Large quantities were dissolved and taken directly into the stream. Seepage was also excessive and much alkali was carried to the lower land by the seepage water. The land was finally drained, but the alkali content of the soil was not reduced since the quantity added was greater than that lost by drainage. Lining the canal through the alkali-charged shale corrected the entire matter. Soil experts and drainage engineers, before deciding on the methods of reclaiming any alkali tract, should discover all probable sources of

the alkali in the area under consideration and select their methods of reclamation accordingly."

Vegetation growing on alkali soil has a characteristic appearance similar to that found growing under desert conditions. It generally lacks that bright green appearance of vigorous and healthy growth, even in water-logged land where there is an ample supply of moisture. When alkali salts are present in sufficient concentration, the transpiration is reduced very much. "It is highly desirable that the prospective land owner should, by studying the trees, shrubs, and grasses, be able to say that the soil is deep, well-drained, fertile, free from injurious properties, and capable of producing profitable crops. Upon many soils the native plants tend to group themselves to the exclusion of nearly all other species. Generally when such grouping occurs, there is some peculiarity of the soil which is made evident by such grouping. The luxuriant growth of one species of plant to the exclusion, or the near exclusion, of other species affords an excellent index to the nature of the soil."

The real remedy for alkali soil is suitable drainage, p. 167. "During the early years of irrigation in America no provision was made to remove the excess water that always collects in the lowlands of irrigated districts. This is one of the chief reasons for the accumulation of alkali. The modern up-to-date irrigation system should include some method of drainage whereby any excess of water is carried out of the land; for there are always a few farmers who, to the detriment of themselves and their neighbors, use too much water. A drainage system laid out at the same time as the irrigation system will in some cases be more simple than one installed after the land becomes a bog. In swampy places drain ditches are constructed with difficulty and tile cannot be laid evenly and securely. Unfortunately, the reclamation of most alkali land is not undertaken until after the condition has become bad. This means that many difficulties are encountered. Of course it would not be wise to install drainage when the irrigation system is put in unless there is likelihood of water-logging. The problem is doubly complex since not only must excess soil water be removed but the alkali must also be washed out.

"Where drainage systems are installed on land there is generally a complete transformation; many conditions favoring crop growth are improved Most important in an alkali soil is the removal of the excessive salt. In many soils where the salt content is not high enough to prevent crop growth, there is sufficient to reduce the yield to a point that is unprofitable. The expenses are practically the same in raising half a crop as a full one. In the one case farming is carried on at a loss, and in the other a good profit may be realized. Thus, removing alkali by drainage may make highly productive millions of acres of land that is only moderately successful. There are also millions of acres at present wholly unproductive that may be made to yield bounteously by removing the alkali.

"Drainage removes the excessive water from the soil. By lowering the water-table the plant is given a larger root zone from which to draw both food and water. If only the surface foot or two can be drawn on for food the plant cannot be expected to be so well supplied with nourishment as it would with a feeding area of five or six feet "

It is unfortunate that the most tolerant cultivated crops are not well

adapted to grow in the climate of most parts of the United States where alkali is found. The date palm, which is perhaps the most tolerant crop for soils containing chloride and sulphate salts, rice, cotton, berseem clover, and several other desirable crops are adapted only to the waimer alkali regions. Australian salt-bush, which withstands larger quantities of alkali than almost any other desirable alkali-resistant plant, does not do well where winters are severe. Forage crops have given more satisfaction for use on rather strong alkaline soils than other cultivated crops as a general rule. Quality in fruit, vegetable, sugar, fibre, and grain crops is frequently so impaired by alkali that the crop is practically worthless for the product ordinarily obtained; but since quantity is the chief requisite for forage the crop serves its purpose when a good yield is obtained.

The author has arranged his material under the following headings· introductory geographical distribution; the origin of alkali; nature of alkali injury to the plant; toxic limits of alkali, native vegetation as an indicator of alakli; chemical methods of determining alkali; chemical equilibrium and antagonism; relation of alkali to physical conditions in the soil; relation of alkali to biological conditions in the soil; movement of soluble salts through the soil; methods of reclaiming alkali lands, practical drainage, crops for alkali land; alkali water for irrigation; judging alkali land *Wilder D. Bancroft*

Introduction to General Chemistry. *By H Copaux. Translated by Henry Leffmann 18 × 12 cm; pp x + 195 Philadelphia: P. Blakiston's Son and Co, 1920* --In the preface the translator points out that Professor Copaux's work presents in compact, yet clear, form a large amount of information on the principles of chemistry as recognized to-day by the leaders in the science. The book gives in a condensed form a great many of the principles of physical chemistry and, as such, is a distinct addition. The reviewer is not certain that it can be read with profit by students just beginning chemistry. He would be more inclined to recommend it to teachers of chemistry and yet for them there are some things which are superfluous. Almost anybody can find something of value in the book and yet it does not fit in anywhere An American translator should have known that Wolcott Gibbs did not deduce the phase rule, p 139, and the reviewer canno agree with the foot note, p 151, added by the translator that the term "enzyme" is now used largely as a substitute for the word "catalyst" It is not true that the conducting power of a sodium chloride solution increases with dilution, p 88. It is the moleculai conductance which increases. *Wilder D. Bancroft*

THE OXIDATION AND LUMINESCENCE OF PHOSPHORUS. II

BY HARRY B. WEISER AND ALLEN GARRISON

The Energy Emissions from Oxidizing Phosphorus

The oxidation of phosphorus is probably the most widely studied chemiluminescent reaction. In addition to the emission of light investigators have claimed that oxidizing phosphorus and phosphorus trioxide emit gaseous ions, radiations that penetrate black paper and metallic films, and a so-called "emanation" that is condensed by liquid air. For the sake of clearness in presentation, the question of the different kinds of emissions will be considered both historically and experimentally in separate sections as follows: gaseous ions; penetrating radiations; phosphorus emanation; and light.

Gaseous Ions

It has been known for a long time that air which has passed over phosphorus at not too low a temperature has the power of discharging both positively and negatively charged bodies.[1] Among the earlier investigators of this interesting phenomenon may be mentioned Naccari,[2] Bidwell,[3] and Elster and Geitel.[4] The last-named investigators attributed the conductivity of air in the region of glowing phosphorus to the process which results in ozone formation. They showed, however, that the mere presence of ozone was insufficient to account for the phenomenon.

Ten years after Elster and Geitel recorded their observations Barus[5] carried out some experiments to determine whether the ionizing properties of air passed over phosphorus could be exerted through thin films of various materials. He

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[1] Matteucci: Encyclopedia Britannica, **8**, 622 (1855).

[2] Atti Sci. Torino, **25**, 252 (1890).

[3] Nature, **49**, 212 (1893).

[4] Wied. Ann., **39**, 321 (1890).

[5] Experiments with Ionized Air, Washington (1901); Am. Jour. Sci., [4] **12**, 327 (1901).

found that he could get no appreciable effect with any films except those prepared from thin tissue paper; and with these, it seemed probable that the effect made its way through the pores of the paper since the transmission ceased when the pores were closed by oiling the paper. Barus found further that air passed over phosphorus was a very active cloud producer, whereas hydrogen passed over phosphorus was not a conductor of electricity and contained no nuclei on which moisture condenses.

Helmholtz and Richarz[1] observed the condensation of a steam jet in the presence of slowly oxidizing phsophorus; and the effect was not diminished when the luminous vapor was blown aside. Such an effect is produced by gaseous ions[2] and indicates their presence in the region of oxidizing phosphorus.

Van't Hoff[3] attributes the activity of phosphorized air produced by slow oxidation to the formation of oxygen atoms or oxygen ions. He placed a small amount of phosphorus in a solution of indigo-sulphuric acid and shook. After each shaking a flame appeared that quickly died out. Nine milligrams of phosphorus had not disappeared entirely after the flame had returned 277 times. From the results of this experiment he says: "The primary product formed by the oxidation of phosphorus is not ozone. According to the above-mentioned phenomena something is present in the atmosphere of the vessel which prevents the phosphorus from oxidizing; there is apparently enough oxygen left; there might be supposed to be a deficiency of phosphorus vapor. That such is not the case is proven by the appearance of a luminescence in contact with air. According to the investigations of Chappuis, ozone favors the luminescence. On shaking with indigo the hampering action which I am inclined to ascribe to the electric charge,—to the excess positive and negative oxygen ions—is destroyed, whereas sulphuric acid, perhaps

[1] Wied. Ann., 40, 192 (1890).

[2] C. T. R. Wilson: Phil. Trans., 192, 403 (1899); J. J. Thomson: Phil. Mag., [5] 46, 528 (1898).

[3] Zeit. phys. Chem., 16, 411 (1895).

on account of its conductivity, accelerates it to a high degree. That the act of shaking, which enables the oxidation to take place again, cannot be attributed to saturating with phosphorus vapor, is shown by the fact that without indigo, with phosphorus and water only, the whole of the typical flame phenomenon is not produced."

In speaking of these ions van't Hoff says: "If the parts in question are charged positively and negatively, it may be easily understood that the substance which is oxidized prefers one of them while the other gives an electric charge to the oxygen which ends in the formation of ozone, the decolorization of indigo, etc."

The above view is not shared by Schenck,[1] who believes that electrons are formed during the oxidation of phosphorus and that these transform oxygen into ozone. He supposes an equilibrium to arise between oxygen, ozone and oxygen atom ions that may be formulated as follows:

$$O_2\overset{+e}{O^{+e}} + 2\,(-e) \rightleftarrows O_3$$

in which $\overset{+e}{O^{+e}}$ represents an oxygen atom and (—e) an electron. Jorissen[2] has shown that the above hypothesis is not in accord with the experimental facts.

Baker[3] obtained experimental results which indicate that oxygen ions are formed during the oxidation of phosphorus: "He took three similar bits of glowing phosphorus, placed them in lead tubes and over them a photographic plate in the dark. He wanted to measure the amount of light given out by these pieces of glowing phosphorus. One tube was charged negatively from a large accumulator; another was charged positively; and a third was left uncharged. The phosphorus was just moist enough to become a conductor. He left it about half an hour and then developed the plates; under the positive tube he found a black mark, under the negative scarcely any; and the third was about the mean of the other

[1] Sitzungsber. Akad. Wiss., Berlin (1904).
[2] Chem. News, 92, 62 (1905).
[3] Jour. Soc. Chem. Ind., 24, 481 (1905).

two. That was only one experiment and many more would be required to confirm the observations. It seemed to him that this experiment, which of course required confirmation, might throw some light on the question as to whether ions were really produced, the positive ions of oxygen being attracted to one side and the negative ions to the other. There were very few positive ions combining with the phosphorus; what became of them? They all knew that ozone was produced when phosphorus glowed. He did not measure the ozone coming from each piece of phosphorus; but, if the hypotheses formed were correct, he would find little ozone at the positive phosphorus, while much would be produced at the negative."

Schmidt[1] observed that air in contact with phosphorus was a conductor and he likewise sought to attribute the conductivity to the presence of positive oxygen atoms derived from oxygen molecules; the negative oxygen according to this idea serving for the oxidation of the phosphorus. His experiments lead him to conclude, however, that the conductivity is entirely a convection phenomenon,—the electricity being carried by the particles of vaporized phosphorus, phosphorus pentoxide, etc., and not by gaseous ions. Later[2] he attributes the conductivity to phosphorus acids rather than the anhydrides. He claims that the conductivity ceases if the cloud of particles is blown aside by a suitable current of air.[3] In confirmation of the convection theory Schmidt[4] placed a piece of phosphorus near two metal plates, one of which was charged and the other connected with an electrometer. He noted that the fog of particles emanating from the phosphorus changes its normal direction under the influence of the electric force and is attracted to the nearer of the two plates irrespective of whether it is charged positively or negatively. From this he concluded that the presence of gaseous ions is improbable.

[1] Phys. Zeit., 3, 475 (1902).
[2] Ibid., 4, 293 (1903).
[3] Cf. however, Helmholtz and Richarz: Loc. cit.
[4] Drude's Ann., 10, 704 (1903).

Schmidt's conclusion has been apparently disproven by the results of a number of investigators among whom may be mentioned Harms, Bloch, Elster and Geitel, Blanc and Jorissen. Harms[1] showed that the conductivity of the air disappeared much more rapidly than the cloud of pentoxide particles settled and that a very dense cloud of ammonium chloride did not act as a conductor. Moreover, he was unable to confirm Schmidt's experiment that a cloud of vapors from glowing phosphorus always moves to the nearest electrode irrespective of the charge on the electrode. A small cloud was formed by blowing moist air over phosphorus and this was allowed to fall between the two plates of a condenser. When a potential difference was applied the cloud divided equally and flowed down both plates. This division of the cloud took place irrespective of whether the cloud was directly in the middle between the two plates or nearer to one of them. The difference between this experiment and Schmidt's is that the latter brought a piece of solid phosphorus into his apparatus. Harms points out: "Since complete insulation is impossible in an atmosphere filled with the products of the oxidation of phosphorus and water vapor, the piece of phosphorus forms part of the inner wall of the vessel connected to the earth and this wall always acts as an electrode in Schmidt's arrangement. In a stream of air rising from an electrode there can be only ions of the same charge so that in these cases the cloud stream must wander to the other electrode. Moreover, the motion of a cloud in an electric field can be accounted for according to Zeleny[2] without having to assume a charging of the cloud particles: the ions by their movement produce an air current which drags along the cloud particles."

Harms made a study of the effect of varying electromotive force on the strength of the current passing through phosphorized air and claims that his results prove conclusively that ions are present. From measurements of the strength

[1] Phys. Zeit., 4, 111, 436 (1903).
[2] Proc. Camb. Phil. Soc., 10, 14 (1898).

of the saturation current, he estimates the ratio of the number of oxidized oxygen molecules to the number of ions formed by the oxidation of phosphorus. He concludes that ions begin to be formed only after eight million oxygen molecules have taken part in the action[1] and hence that ionization is due not directly to the oxidation process but depends on the formation of ozone by secondary reactions. In this connection it is interesting to note that Richarz and Schenck[2] showed that decomposing ozone actually gives ions. However, decomposing ozone cannot be the only source of ions since Gockel[3] claims that ozone may be removed from phosphorized air without destroying the conductivity. This conclusion was confirmed by Meyer and Müller.[4] The latter showed further that ionization was not due to the light emitted during the oxidation: A piece of phosphorus was allowed to oxidize in a very thin-walled quartz vessel which was transparent to ultraviolet radiations, but no ionization was detected outside the vessel.

The investigations of Harms were extended by Bloch.[5] The latter passed dry air at constant rate over dry phosphorus and determined the conductivity of the air due to ionization. From his results he calculated the speed of the ions to be one three-hundredth millimeter per second for a fall of potential of one volt per centimeter. The mobilities were thus only about one one-thousandth of that of ions produced by Röntgen rays. The mobilities were found to be greatest close to the phosphorus. These conclusions were confirmed and extended by L. and E. Bloch.[6] Unlike Harms, they concluded that the ions result from the vivid oxidation reaction in the same way that other cases of rapid combustion yield ions. The speeds of the ions in phosphorized air are of the same order of magnitude as that of other ions formed by chemical action

[1] Cf. Rinde: Ark. Kem. Min. Geol., **7**, 21 (1917–18).
[2] Sitzungsber. Akad. Wiss., Berlin, 1102 (1903).
[3] Phys. Zeit., **4**, 602 (1903).
[4] Verh. deutsch. phys. Ges., **2**, 332 (1904).
[5] Comptes rendus, **135**, 1324 (1902); Ann. Chim. Phys., [8] **4**, 25 (1903).
[6] Comptes rendus, **147**, 842 (1908).

and indicate that the ions are of considerable size. The Blochs found mobilities as high as 0.1 mm per second under a fall of potential of 1 volt per centimeter close to the phosphorus. Values as high as 2 to 3 mm were obtained by screening out the fumes which condense on the ions rendering them heavy and so decreasing the mobility. Bloch[1] has determined also the value of α, the coefficient of recombination of the ions in phosphorized air and found that this too was one one-thousandth of the α for ions produced by Röntgen rays. The ratio ϵ of the number of recombinations to the total number of collisions between ions of opposite sign, lay between 0.7 and 1. All the independent measurements of mobility, of α and of ϵ gave concordant results indicating true ionization. Moreover, Bloch has shown that the conductivity can be taken out of phosphorized air by making it pass through a strong electric field,—a property characteristic of an ionized gas.

The investigations of Elster and Geitel,[2] Jorissen and van Reesema[3] and Blanc[4] give additional confirmation of the presence of ions in phosphorized air and so disprove Schmidt's convection theory to explain the conductivity.[5] Blanc has studied the effect of an electric field on the oxidation of phosphorus by coating one electrode with a layer of vaseline 0.25–1.0 mm thick mixed with a solution of phosphorus in carbon bisulphide. He observed that the strong oxidation which takes place at first soon decreases and in a short time becomes uniform. When placed in an electric field the oxidation increases and the fumes which have disappeared are again evolved. This observation is explained by the fact that the ions which are the product of the oxidation are removed by the field as they are formed, thus favoring oxidation. The curve showing the intensity of ionization as a function of the field shows a concavity toward the axis representing the

[1] Comptes rendus, 137, 1040 (1903).
[2] Phys. Zeit., 4, 457 (1903).
[3] Chem. Weekblad, 6, 931 (1909).
[4] Comptes rendus, 152, 1170 (1911); 158, 1492 (1914).
[5] Cf. however, Schmidt: Ber. deutsch. phys. Ges., 4, 640 (1906).

intensity, indicating that the latter increases more rapidly than if it obeyed Ohm's law. When the phosphorescent layer has aged to such an extent that the oxidation is quite feeble, the curve corresponds to one of complete saturation.

Experimental

From the evidence above recorded, there seems little doubt but that gaseous ions are formed during the oxidation of phosphorus. However, the study of this reaction by different investigators has led to a number of conflicting observations which suggested the experiments which will now be considered.

The effect of an electric charge on the luminosity of phosphorus.—It will be recalled that Baker carried out experiments which seemed to indicate that phosphorus glowed less brightly when positively charged than when negatively charged. In order to determine whether or not any change in the intensity of the luminescence is produced by charging the element, the following experiments were carried out:

Experiment 1.—Two circular lead discs three centimeters in diameter were placed on sulphur blocks to insulate them and were connected by fine copper wires to terminals of a static machine. A small lump of phosphorus was placed on each disc, the lumps possessing as nearly as possible the same size and shape. Since the air above the plates was ionized, the charge leaked slowly off the phosphorus. By altering the speed of the static machine, the potential could be varied from a few volts to several thousand. Over this wide range of potential no change in intensity of luminescence could be observed with the eye. It was thought that the difference in intensity recorded by Baker might have been due to penetrating emissions to which a photographic plate was sensitive. Therefore a photographic plate was protected from light by black paper and supported on sulphur plugs so as to be an equal distance, 5 mm, from each piece of phosphorus charged as above described. Experiments were performed with potentials varying from six volts, maintained by a storage battery, to several thousand volts, maintained by a

static machine. In a series of six experiments each with varying periods of exposure, results were obtained from which no definite conclusions could be drawn. The action on the plate was irregular in outline; but so far as could be judged the amount of fogging was equal for both positive and negative pieces.

Experiment 2.—For reasons to be discussed in the next section it seemed likely that more conclusive results would be obtained by protecting the plates from the gaseous products of the oxidation of phosphorus. This was accomplished in the following way: Metal plates were placed parallel and horizontal about 7 mm apart. The lower plate consisted of three parts, which will be referred to as A, B and C, insulated from each other and covered by a sheet of black paper in which were cut three small holes, one over the center of each section. Lumps of phosphorus of uniform size, cut from a small stick of the element, were placed over the holes in the paper making contact with the metal plates. Three holes 2.0 cm in diameter were cut in the top metal plate above the lumps of phosphorus; and cylinders of black paper 2 cm high inserted. These cylinders were closed at the top by thin microscope cover-glasses, in order to protect the photographic plate from oxidation products. The upper plate and the middle section of the lower plate B were earthed and connected to the middle point of a battery of 100 small lead cells. One end section A of the lower plate was connected to the positive terminal of the battery; and the other end section C to the negative terminal. The electric intensity at each piece of phosphorus was roughly 100 volts per centimeter upward at A; 0 at B; and 100 volts per centimeter downward at C. This apparatus was placed in a dark room and a photographic plate exposed above the lumps of glowing phosphorus. Nine exposures were made, varying in time from 1 to 40 seconds. For each exposure the three circular discs formed on the plates were identical in intensity as nearly as could be determined. The plates exposed for one second showed three very faint discs; while those exposed for 40 seconds showed three very

dark ones. There was no indication whatsoever of the differences in intensity recorded by Baker.

Although differences in the rate of oxidation of charged and uncharged phosphorus are not sufficiently marked to be detected photographically, Blanc has shown by a much more sensitive method, that an electric field actually increases the oxidation of the element. This conclusion is in accord with what one might expect from the behavior of the oxidation products in an electric field. In the above experiments it was observed repeatedly that the oxide fumes tended to cling about the surface of an uncharged piece of phosphorus; whereas when the element was placed in an electric field, the cloud of particles moved away from the surface,—a circumstance that favored oxidation.[1]

The nature of the charged cloud.—The condensation of water vapor on gaseous ions is a well known phenomenon. It has been pointed out that the experimental evidence seems to indicate that the ions involved when phosphorus oxidizes are clusters of oxide molecules about a charged nucleus. It is only a step in the development of this theory to assume a condensation of water vapor on such a cluster, producing a charged cloud. H. A. Wilson[2] has shown in a rather direct way the influence of minute traces of soluble substances in promoting cloud formation over water.

It has been shown that both positive and negative ions are present when phosphorus oxidizes and that their mobilities are approximately the same. From an uncharged lump of phosphorus we would thus expect to find a cloud containing particles both positively and negatively charged, while from a lump of charged phosphorus we would expect all the ions to have the same charge as the element. These conclusions have been proven as follows:

Experiment 3.—Two parallel plates were placed 3 cm apart and charged oppositely by a set of cells giving 150 volts. A small lump of phosphorus was mounted on a metal

[1] Cf. Weiser and Garrison: Jour. Phys. Chem., **25**, 61 (1921).

[2] Phil. Mag., [5] **45**, 454 (1898).

point midway between the plates. When the metal point bearing the phosphorus was connected to one of the charged plates, the fumes moved to the opposite plate irrespective of the signs. When the phosphorus was neutral part of the fumes moved to each plate. This has been demonstrated more satisfactorily by directing the fumes from a piece of phosphorus between two oppositely charged plates. A division of the cloud occurred exactly as described by Harms.

The results above described afford additional confirmation of the theory that the conductivity of phosphorized air is due to ions.

The source and nature of the ions.—A number of suggestions have been offered to account for the existence of ions in phosphorized air. The ionization may result from: (1) the direct oxidation of phosphorus or phosphorus trioxide; (2) a secondary action involving the formation of ozone; (3) the decomposition of ozone; (4) the action of ultraviolet light emitted by the reaction. As previously pointed out, Richarz and Schenck showed that decomposing ozone yields ions; but Gockel claimed to eliminate ozone decomposition as an important source of the ions by showing that the conductivity of phosphorized air passed through three wash-bottles containing potassium iodide solution, was still "at least twice as great as the air of a room." It would seem that this experiment alone scarcely justified the conclusion that the ions in phosphorized air were not due to decomposing ozone. What Gockel showed was that the ionization beyond the wash bottles was not due to ozone; but he failed to show whether this ionization came from the phosphorized air or from bubbling the air through a solution,—a well established source of electrification of air.[1] Moreover, Schmidt claimed that the conductivity disappeared when the oxidation products including ozone, were blown aside. The following experiments bear on these points:

Experiment 4.—To study the behavior of the ions from

[1] Kelvin: Proc. Roy. Soc., **57**, 355 (1894); Thomson: Phil Mag., [5] **37**, 341 (1894); Kelvin, Maclean and Galt: Phil. Trans., **191A**, 187 (1898).

oxidizing phosphorus in an electric field, the apparatus shown in Fig. 1 was employed. This apparatus consists essentially of a Wilson tilted electroscope. The case of the instrument A was earthed; the plate B was connected through a battery of cells to the earth; the needle C could be charged and observed through a microscope attached to the instrument. The electroscope E was a brass rod encased in a shield D which

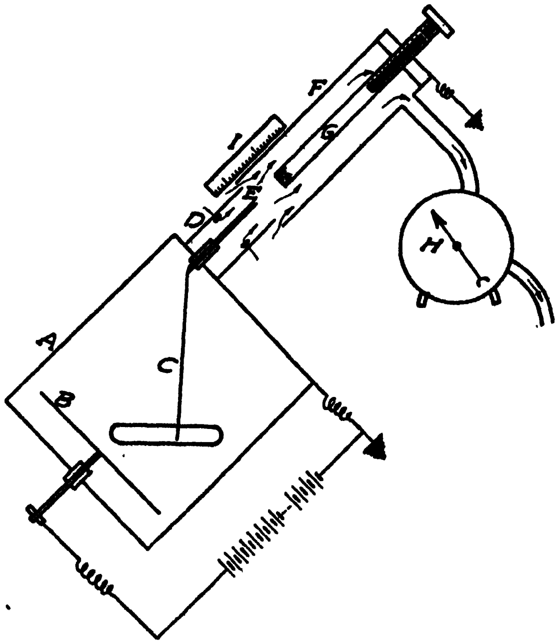

Fig. 1

was perforated with several holes to permit a free circulation of air. This electrode was charged to a potential of 150 volts. A glass tube F was clamped so that electrode E was symmetrically placed in it. By drawing air through the flowmeter H a uniform current was obtained as is indicated by the arrows. A piece of phosphorus, 3 mm in diameter, was placed in a brass tube G which was earthed to the case of the instrument. The distance of the phosphorus from the electrode E was adjusted

by rotating the thumbscrew at the top of G; and this distance was read on the scale I. The air current was so regulated that the cloud of oxidation products was carried up the tube F as rapidly as formed. In this particular apparatus the desired results were obtained by a rate of 0.01 cubic foot per second. Readings were made as follows: The phosphorus was set at the desired distance from the electrode; the air current regulated; and a number of readings taken of the time required for the foil to traverse 50 divisions on the microscope scale. The maximum variations in time for the different distances are recorded in Table 1.

TABLE 1

Distance of phosphorus from electrode (mm.)	Maximum variation in time (sec)
2	5 to 6
3	9 to 11
4	15 to 17
5	21 to 23
6	40 to 45
7	80 to 85
8	140 to 150
9	280 to 300
10	520 to 500
11	1450 to 1550
12	2250 to 2750

It will be noted that under the conditions of the experiment ions are drawn from the phosphorus against the air current to a distance of a centimeter or more. Since the leak of the electroscope is approximately proportional to the number of ions present, their number for short distances is roughly inversely proportional to the square of the distance. Since the products of the reaction, oxides, acids, ozone, and hydrogen peroxide, are swept away in the air stream as fast as formed it is quite evident that the existence of none of these oxidation products is essential in imparting conductivity to the air.

The question which next presents itself is the effect of increasing the rate at which air is drawn past the glowing phosphorus. Since the results of the above experiment seem to confirm Bloch's conclusion that the ions are formed as the result of the energetic oxidation and may be drawn from the reacting zone, it follows that increasing the air rate should increase the velocity of oxidation and hence the concentration and mobility of the ions. Opposing this effect is, of course, the increased air rate which would tend to slow down the ions. That the latter effect is slight compared to the former is shown by the results of the following experiment.

Experiment 5.—The method of procedure followed in this experiment is similar to that described in the preceding one. The distance of the phosphorus from electrode E was held constant at 5 mm and the time of leak of the electroscope over 50 scale divisions was determined for different rates of air current. The results are given in Table 2 which is self-explanatory.

TABLE 2

Time of flow of 1 cu. ft. of air (sec.)	Rate of leak of electroscope division per sec.
150	60 to 65
70	48 to 50
39	40 to 42

The effect of ultraviolet light.—Since ultraviolet light is emitted by the oxidation of phosphorus it is not impossible that this light produces the ionization of the air.[1] This was tested in the following way:

Experiment 6.—A piece of glowing phosphorus was held near one side of a clear quartz glass plate 1 mm in thickness; and an attempt was made to detect the presence of ions on the opposite side of the plate by means of a Wilson tilted electroscope. No ions whatsoever could be detected at a

[1] Hertz: Wied. Ann., **31**, 983 (1887); Elster and Geitel: Wied. Ann., **38**, 40, 497 (1889); **41**, 161 (1890); **42**, 564 (1892); **43**, 225 (1892); **45**, 433 (1894); **45**, 684 (1895); Wilson: Phil. Trans., **192A**, 493 (1899).

distance less than 1 mm from the plate. This result indicates that ionization from the ultraviolet light emitted by the oxidation of phosphorus is inappreciable.

Summary.—The results of the series of experiments just described show: (1) that the luminescence of phosphorus is not altered appreciably by charging the element; (2) that the cloud arising from moist, glowing phosphorus contains equal amounts of positive and negative particles providing the element is not charged; (3) that ions are formed in the zone of reaction and may be readily drawn out by an electric field against a current of air sufficiently rapid to remove the cloud of oxide particles, ozone, and hydrogen peroxide; (4) that the decomposition of ozone and the action of ultraviolet light are unimportant as sources of ions in phosphorized air.

Penetrating Radiations

Knoblauch[1] first observed that "phosphorus like uranium causes a photographic radium-like action which also penetrates through untransparent substances." This behavior was rediscovered by Jorissen,[2] who observed that a photographic plate was darkened by an emission that apparently penetrated not only black paper but thin films of mica, gold and silver.

Contrary to the above observations Schmidt[3] found that a photographic plate protected by an aluminum envelope was not acted on by glowing phosphorus. Centnerszwer and Petrikaln[4] showed further that the action on the plate observed by Jorissen was not due to a penetrating radiation since a plate covered with one thickness of black paper was not darkened after 40 hours exposure provided the oxidation products were removed as fast as formed. They conclude that the fogging of a plate through black paper was due "to the direct action of a so-called phosphorus emanation that is either a gas or some substance suspended in a gas which results from the oxidation. Recently many examples of the action of dif-

[1] See Bredig and Pemsel: Arch. wiss. Photographie, **1**, 33 (1899).
[2] Chem. Weekblad, **1**, 341 (1904); Chem. News, **96**, 62 (1905).
[3] Drude's Ann., [4] **10**, 704 (1903).
[4] Zeit. phys. Chem., **80**, 235 (1912).

ferent materials on the photographic plate have been studied. In almost every case it has been shown that we are not dealing with the effect of rays but with a direct chemical action of some substance. In most cases hydrogen peroxide has been found to be the substance responsible for the effect on the photographic plate. Since hydrogen peroxide is produced by the oxidation of phosphorus in moist air, it is likely that in this case also the action of this product was erroneously attributed to phosphorus rays."

In a recent communication Jorissen[1] concludes that the negative results obtained by Centnerszwer and Petrikaln were due either to too low a temperature or to too rapid a current of air passing between the enveloped photographic plate and the phosphorus. With an apparatus similar to that described by Centnerszwer and Petrikaln, Jorissen obtained an action on a plate through black paper. However the method used by Jorissen to withdraw the products of oxidation would seem to be unsatisfactory. When the fumes were removed as Centnerszwer and Petrikaln did, by passing a current of air between the plate and the phosphorus, Jorissen observed that "according to the velocity of the current of air, it was possible to obtain or not to obtain an action on a photographic plate."

Experimental

The question of phosphorus rays.—To determine the accuracy of Centnerszwer's conclusion the following experiments were carried out:

Experiment 1.—Three 150 cc beakers were set side by side and small lumps of phosphorus of uniform size were placed in each. The first beaker was left open; the second had a lead plate which entirely covered the phosphorus in it but allowed free access of air; and the third was supplied with a disc of lead foil containing a small hole. This disc, which fitted the sides of the beaker snugly, was placed about 1 cm from the top of the beaker. A photographic plate in an envelope of black paper was placed face down over the three beakers and left for 24 hours. When the plate was de-

[1] Rec. Trav. chim. Pays.-Bas., **39**, 429 (1920).

veloped it showed three black discs of equal intensity having the same diameter as the beakers. It is evident that the light emitted by the glowing phosphorus has no influence on the plate through the paper, for in the first beaker all the light struck the plate; in the second none of the light struck the plate; and in the third only a small hole was open to admit light. And yet the fogging was the same in every case. There is no doubt but that the fogging was due to vapors which diffused through the paper rather than to penetrating rays.

Experiment 2.—The experiment of Centnerszwer and Petrikaln was repeated as Jorissen did taking particular care to remove the products of oxidation with such a slow current of air that it increased rather than decreased the rate of oxidation. The procedure was as follows: A lead disc was cut to fit snugly in a brass tube 5 cm in diameter. Before putting the disc in place it was perforated with a number of holes 2 mm in diameter. A disc of phosphorus the same size as the lead disc was next prepared and punctured with holes that coincided with those in the lead plate. The phosphorus was pressed firmly against the lead approximately 3 cm from one end of the brass tube. Gentle suction applied at the other end of the tube removed the products of oxidation as fast as formed. A photographic plate enclosed in an envelope of black paper was placed over the end of the brass tube three centimeters from the glowing phosphorus. After 4 hours exposure the plate was developed and it was not fogged in the least. The temperature of the room was 23° and the phosphorus glowed throughout the experiment. The results confirm those of Centnerszwer and Petrikaln and indicate that Jorissen's method of removing the fumes was inadequate.

Centnerszwer has pointed out that the effect of phosphorized air on a photographic plate is probably due to the action of hydrogen peroxide formed when moist phosphorus oxidizes slowly. Since some phosphorus trioxide is formed during the oxidation of phosphorus under certain conditions, experiments were carried out to determine whether the vapors

of this oxide would affect a photographic plate through black paper.

Experiment 3.—Phosphorus trioxide was prepared by the method of Thorpe and Tuttle,[1] using particular care to prevent contamination by phosphoric oxide or phosphorus. The low boiling oxide was redistilled twice in an atmosphere of hydrogen and a perfectly white product was obtained that melted sharply at 22.5°. The preparation was kept in a small, glass-stoppered, hydrogen-filled bottle which was opened only in an atmosphere of hydrogen.

A small photographic plate was wrapped in black paper and placed in a jar filled with hydrogen. On the paper were sprinkled a few crystals of the trioxide which were allowed to remain for a few minutes after which the plate was developed. Fogged spots on the plate indicated chemical action of the fumes of the oxide on the emulsion. In order to show that the effect was not due to a product formed by the action of moisture on phosphorus trioxide,[2] a plate wrapped in black paper was placed in a jar containing phosphorus pentoxide which was subsequently filled with hydrogen dried by the pentoxide. A few crystals of trioxide were sprinkled on the paper covering the plate and after a few minutes the plate was removed and developed. Particular care was taken to prevent the action of moisture or oxygen on the oxide while removing the plate from the jar. A marked fogging was obtained exactly as in the previous case.

Summary.—Radiations of the nature of radium rays, which penetrate black paper and thin metal plates, are not formed during the oxidation of phosphorus. The darkening of a photographic plate protected from light in the region of glowing phosphorus is due to the action of the vapors of hydrogen peroxide and phosphorus trioxide.

Phosphorus Emanation

Schenck, Mihr and Banthein[3] showed that phosphorus

[1] Jour. Chem. Soc., **57**, 650 (1890).
[2] See the following section.
[3] Ber. deutsch. chem. Ges., **39**, 1506 (1906).

trioxide formed by the action of air on phosphorus is a very energetic ionizing agent. Later Schenck and Breuning[1] sought to show that this ionizing action is due to a so-called phosphorus emanation produced by the action of moisture on phosphorus trioxide. Their method of procedure and results are as follows:

Air was first dried thoroughly by passing it through a U-tube *a* immersed in liquid air and was then conducted through a second vessel *b* containing phosphorus trioxide. The vapors were led into the chamber of an electrometer supplied with a diaphragm that was intended to prevent an acid cloud from coming in contact with the insulation and so destroying it. No deflection of the electrometer needle was observed, thus confirming Scharff's observation that perfectly dry air does not oxidize phosphorus trioxide. In a series of experiments that followed, nitrogen and hydrogen were substituted for air. With these gases also no effect was observed until moisture was added. An example of their data using hydrogen gas is given in Table 3. In Experiment 1, both vessels *a* and *b* were immersed in liquid air; in Experiment 2, vessel *a* was in liquid air and *b* at room temperature; in Experiment 3, both vessels were at room temperature, thus allowing both moisture and phosphorus trioxide vapors to enter the electrometer chamber.

TABLE 3

Time of observation (minutes)	Divisions on electrometer scale	Time of observation (minutes)	Division on electrometer scale
Experiment 1		Experiment 3	
0	141.0	0	135.0
60	140.8	5	111.5
Experiment 2		10	98.5
		15	86.5
0	140.8	20	78.5
15	140.0	30	43.0
		50	30.0

[1] Ber. deutsch. chem. Ges., **47**, 260 (1914).

From the above data it is evident that there is no action on the electroscope until both moisture and trioxide are brought together. The authors point out that it takes some time for the discharge to take place; but show that the process can be hastened by heating up vessel *a* rapidly by immersing it in water at room temperature, and so driving more water vapors into the electrometer chamber.

Finally, the authors placed a condensing vessel *c* between the trioxide vessel and the electroscope, and found that there was no discharge of the electrometer as long as *c* was held at —180°. However, a slow discharge took place when *c* was heated to —80° and a rapid discharge when it was brought to room temperature. From these results the following conclusions were drawn:

"1. The ionization of the atmosphere by phosphorus trioxide does not result from an oxidation process but from a reaction of the oxide with water vapor.

"2. The ionization is not produced directly by the process of hydration; but results from a volatile reaction product condensible at —180°, a phosphorus emanation of a nature hitherto unknown."

Experimental

In order to study this so-called emanation further some experiments were carried out that will now be described.

Experiment 1.—Hydrogen from a cylinder was led through two large wash-bottles containing strong alkaline pyrogallol to remove any oxygen and through a preliminary drying column of calcium chloride. It was then passed through a long U-tube A, Fig. 2, immersed in liquid air to remove the last traces of moisture. By rotating stopcock B the dry gas could be passed either directly into U-tube D or through vessel C which contained a few pieces of redistilled phosphorus trioxide prepared as previously described. From D the gas was passed into an electroscope and out into the air. The rate of the leak of the electroscope was taken for pure, dry hydrogen (Experiments 1 and 2, Table 4) and for dry hydrogen containing vapors of phosphorus trioxide (Experiment 3). The

results show the absence of any action. Vessel C was then cut out and dry hydrogen passed through the electroscope to remove any excess trioxide. At this juncture the liquid air was removed from around U-tube A, allowing moisture to enter the apparatus. A strong leak was observed at once which

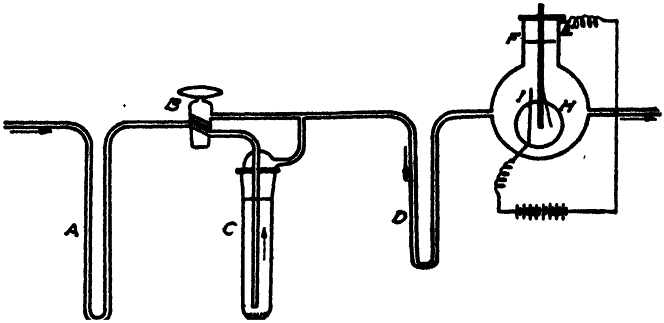

Fig. 2

mounted to 400 scale divisions in 10 minutes (Experiment 4, Table 4). Since the hydrogen in this last experiment did not pass over the trioxide, the leakage was produced by some action of water on the vapors of trioxide condensed on the electroscope and inlet tube. By immersing D in liquid air to dry the hydrogen, the leak was reduced slowly.

TABLE 4

Experiment	Temperature of			Rate of leak Scale division in 10 minutes
	A	C	D	
1	—180°	19.0°	19.0°	6.0
2	—180°	—	19.0°	5.0
3	—180°	19.0°	19.5°	4.5
4	19.5°	—	19.5°	400.0

From the results recorded in Table 4 it was impossible to say whether the leak was due to conduction across the hard rubber insulation plug or through the gas itself. To learn the nature of the conduction the electroscope was modified as

described in Experiment 2, to distinguish between a gaseous leak and an insulation leak.

Experiment 2.—An electroscope was constructed as shown in Fig. 2. A glass vessel of approximately 250 cc capacity was supplied with a needle H. A plate I parallel to the needle was charged positively while a metal cylinder F surrounding the insulation E was charged negatively by a set of cells G. Now, let us assume that the needle receives a positive charge and the leaf shows a certain deflection; if ions are present or any substance producing a gaseous leak, the needle will tend to take up the potential of the plate I and thus will show a greater deflection; on the other hand, if the insulation becomes imperfect, a negative charge will escape from the cylinder F to the needle and the deflection will diminish.

The apparatus, Fig. 2, was first filled with slightly moist hydrogen gas. After some time the needle retained a positive charge and remained fairly steady, the variation being not more than one division on the telescope scale in 10 minutes. Vessel C was then opened for a moment at the ground-glass joint and a small piece of phosphorus trioxide added. This procedure introduced a small amount of air along with the trioxide, so a slight oxidation was to be expected. The leaf of the electroscope was observed carefully and the deflections noted. The results are recorded in Table 5. Since an

TABLE 5

Time (seconds)	Divisions on scale	Time (seconds)	Divisions on scale
0	14	145	35
10	—3	160	39
100	10	175	45
115	25	190	56
130	30	—	—

increase in the number of scale divisions indicates discharge of the leaf, it is evident that at first there is a charging up of the needle from 14 to —3. This indicates a period of short gaseous conductivity which soon disappears, giving place to

a steady leak across the insulation. The gaseous conductivity was due to the slight ionization arising from the slight oxidation at the outset of the experiment.

Experiment 3.—The experiment above described was repeated after removing the trioxide from vessel C and washing the apparatus with hydrogen until the electroscope leak fell below one division in 10 minutes. The results are given in Table 6. In the earlier stages I, the leak is through the gas and is due to ions resulting from the oxidation by air added with the trioxide; after seven minutes have elapsed, the leak is across the insulation as indicated under II; at this juncture the ground-glass joint of C was opened for 5 seconds admitting a little air. The needle is again charged from 31 to 27 as shown under III; but soon resumes its discharge across the insulation since there is such a marked insulation leak in progress.

TABLE 6

I		II		III	
Time (seconds)	Scale divisions	Time (seconds)	Scale divisions	Time (seconds)	Scale divisions
0	15	0	9	212	29
20	14	30	12	215	27
30	10	60	14	230	30
45	9	90	18	260	33
60	9	120	22	290	39
420	9	150	25	—	—
—	—	180	28	—	—
—	—	210	31	—	—

The results above recorded indicate that a gaseous leak is obtained only in the presence of oxygen, while the action of moisture on phosphorus trioxide forms phosphorous acid and causes a leak across the insulation. Schenck and Breuning[1] recognized the destructive action of an acid cloud on the insulation and sought to avoid this by interposing a diaphragm in the electrometer chamber as previously described. While

[1] Loc. cit.

such a diaphragm may prevent the passage of a cloud it should be noted that we are not dealing with a cloud of particles, but with the vapors of the trioxide and water; and a diaphragm which will tend to prevent cloud diffusion may have but little effect in preventing the diffusion of vapors. In order to get an approximate idea of the rate of diffusion of phosphorus trioxide vapors the following experiment was carried out:

Experiment 4.—A small lump of phosphorus trioxide was placed in one end of a tube 0.9 cm in diameter and 150 cm in length. After stoppering the tube, it was clamped vertically and the time noted for the odor of trioxide to be detected at the upper end. But 80 seconds were required.

Although the electrometer used by Schenck and Breuning was 33 cm long and contained a diaphragm, the vapors entering the apparatus probably had to travel less than 40 cm to reach the insulation. This would take but little time as the above experiment shows. Moreover, in the experiments recorded in their paper, Schenck and Breuning apparently passed the dried gas over the trioxide and thence into the electrometer for 15 minutes before adding moisture. It seems to us more than probable that the oxide vapors which readily diffuse condensed on the insulation in Schenck and Breuning's apparatus as it did in our own; and later, in the presence of water vapor, these vapors were converted to acid which occasioned a leak, the rapidity of which varied with the conditions of the experiment. In order to test this conclusion an electrometer was constructed of approximately the same size as Schenck and Breuning's and the following experiments performed.

Experiment 5.—A diagram of the electrometer used in this experiment is shown in Fig. 3. The case of the instrument was of brass 35 cm long and 5 cm in diameter and contained a long brass needle M supported by a hard-rubber plug which was encased in a brass shield K. This shield was also insulated from the case by a rubber ring which closed the end of the electroscope. A long thin strip of aluminum foil was hung at the bottom of the needle. The position of the foil was

observed through glass windows O by means of a microscope with graduated scale. A thin circular mica plate slightly smaller than the diameter of the case was fastened to the needle about 1 cm below the insulation; and just below this a second mica plate fitted the case tightly and had a hole in it through which the needle passed. This formed a diaphragm similar in construction to the one used by Schenck and Breuning. The bottom of the case was supplied with tubes for the inlet and outlet of gases.

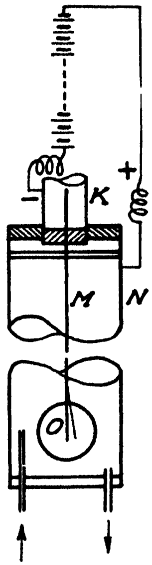

Fig. 3

Hydrogen which had been freed from oxygen by passing through two large wash-bottles of alkaline pyrogallol, was conducted through a wash-bottle containing water and thence into the vessel C, Fig. 2, where it could be passed either directly into the electroscope or over phosphorus trioxide. If there were any ions or charged particles thus introduced into the electroscope, the needle would tend to take up a charge of like sign to that on the case N. If, however, any charge were given the needle due to faulty insulation, that charge would be the same as the charge on the brass ring K. Now if N is made positive and K negative by a battery of cells, the needle may be charged to a potential approximately the mean between K and N and would thus show a deflection in a different direction for each source of charge. With the electroscope arranged in this way a series of experiments were carried out.

Hydrogen was first passed directly into the apparatus until all air was displaced and the needle stood constant. The gas was next passed over the trioxide in C and then into the electroscope. After a time the readings given in Table 7 were taken.

From the following table it will be noted that the needle in the electroscope moved from 42 to 10 scale divisions in three minutes. This motion represents a negative charging of the needle and is thus an insulation leak. If the oxidation of the

TABLE 7

Time (seconds)	Scale divisions	Time (seconds)	Scale divisions
0	42	90	24
15	40	120	19
30	38	150	14
45	31	180	10
60	29	—	—

trioxide should produce ions, any oxygen mixed with the gas would cause a gaseous leak from the case N, or a motion of the needle in the opposite direction. To introduce a small amount of oxygen, the joint in C was opened, allowing a little air to become mixed with the hydrogen as described in Experiment 2 above. The motion of the needle was followed as recorded in Table 8, I. After 5 minutes the leak reversed as shown in Table 8, II. After the twelfth minute oxygen was again admitted and the leak again reversed going off the scale in three minutes, III. The needle was adjusted on the scale and reversed after the ninth minute, IV. Oxygen was admitted at the end of the 20th minute and the needle went off the scale in the reverse direction, V.

The explanation of the results recorded in Table 8 is evident from the arrangement of the apparatus. For a short time after the entrance of oxygen the direction of the motion of the needle shows that a charge is getting from the case N to the needle. This indicates ionization as a result of oxidation. After all the oxygen has been removed and the ions washed out, a leak in the opposite direction takes place showing that faulty insulation has admitted a charge from K. The insulation may be restored to its normal condition by passing a stream of hydrogen through the apparatus for several hours.

After the needle had taken a constant position the experiment was repeated as above described with identical results.

TABLE 8

Time (min.)	Scale divisions	Time (min.)	Scale divisions
I		III	
0	6.0	0	40.0
0.5	15.0	1	42.0
1	22.5	2	48.0
2	32.0	3	55.0
3	39.0	IV	
4	46.0		
5	54.5	5	30.0
II		6	39.0
		8	45.0
6	53.0	9	45.5
7	51.0	10	45.0
8	46.5	11	44.0
9	43.0	12	43.5
10	40.0	15	42.0
11	38.0	20	37.0
12	36.0	V	
—	—		
—	—	21	47.0
—	—	22	53.0
—	—	23	off

Summary.—The action of oxygen on phosphorus trioxide produces a true ionization of the surrounding atmosphere. No evidence was obtained of the formation of a phosphorus "emanation" by the action of moisture on phosphorus trioxide. The vapors of the oxide diffuse readily and when admitted to an electrometer they diffuse throughout the instrument and condense on the insulation. In the presence of water vapor the oxide is converted into acid which causes a leak across the insulation that might be mistaken for a gaseous leak resulting from ionization.

Light

The oxidation of phosphorus has long been cited as a typical chemiluminescent reaction. Since phosphorus burns readily to the pentoxide, it has usually been taken for granted that the luminescence resulted from the reaction: $2P + 5O_2 =$

P_2O_5. It is well known, however, that phosphorus forms a trioxide which can be prepared along with the pentoxide when phosphorus is burned in air under certain conditions.[1] It is probably true, therefore, that the complete oxidation of phosphorus occurs in at least two steps, the trioxide being the intermediate product. The natural inquiry to make is whether both of these steps are equally concerned in the production of the luminescence or whether but one step is so concerned, and if so, which one. As pointed out in a previous communication,[2] Thorpe and Tuttle have shown that the oxidation of the trioxide is accompanied by a luminescence that is quite similar to that produced by the oxidation of phosphorus. Thorpe[3] states that the luminescence of phosphorus is due to the reaction of oxygen with the vapors of phosphorus and phosphorus trioxide. He thus implies that the reaction: $4P + 3O_2 = P_4O_6$ emits light. Jungfleisch[4] has investigated the luminescence phenomena from this point of view and has come to the conclusion that the luminescence of oxidizing phosphorus is due almost entirely to oxidation of the vapors of P_4O_6. This conclusion is based on the observation that the vaporization of phosphorus is altogether too small at ordinary temperatures to account for the marked luminescence.

Although subsequent investigators have shown that Jungfleisch is probably right in his conclusion, his reasoning is not sound. While it is true that the vapor pressure of phosphorus is low at ordinary temperatures, the oxidation reaction is such an energetic one that the temperature is probably quite high in the zone of reaction close to the phosphorus.

Schenck, Mihr and Banthein[5] likewise ascribe the luminescence of phosphorus to oxidation of the intermediate oxide,—a conclusion that is supported by an extended investigation carried out in Schenck's laboratory by Scharff.[6] Thorpe

[1] Thorpe and Tuttle: Jour. Chem. Soc., 57, 650 (1890).
[2] Weiser and Garrison: Loc. cit.
[3] Chem. News, 61, 140 (1890).
[4] Comptes rendus, 140, 444 (1905); 145, 325 (1907).
[5] Ber. deutsch. chem. Ges., 39, 1506 (1906).
[6] Zeit. phys. Chem., 62, 79 (1908).

and Tuttle found that P_4O_6 like phosphorus shows the phenomenon of intermittent luminescence under certain conditions and that at ordinary temperatures there is a definite "glow pressure" of oxygen above which the oxide does not luminesce. Scharff has confirmed and extended these results and has shown further that gases and vapors which prevent the glowing of phosphorus likewise prevent the luminescence of P_4O_6. The marked similarity in the behavior of glowing phosphorus and phosphorus trioxide led Scharff to the conclusion that the luminescence of the element is due to the oxidation of the intermediate oxide. It should be pointed out, however, that the phenomena accompanying the two oxidation processes are not identical. As previously noted,[1] the glow pressure of phosphorus trioxide is not a boundary pressure in the same sense that such exists for elementary phosphorus, since the oxidation of P_4O_6 apparently does not cease entirely[2] at any pressure—due probably to the fact that the formation of a coherent film of pentoxide is prevented on account of the much higher vapor pressure of the oxide than of phosphorus under the same conditions. Moreover, it has been shown that the "glow pressure" obtained by reducing the oxygen pressure until the substance just starts to glow is considerably higher for phosphorus than it is for phosphorus trioxide at the same temperature. For example, at 20° the glow pressure was found by Scharff to be approximately 570 mm for phosphorus and 435 mm for phosphorus trioxide. This latter observation is what we might expect when we consider the fact that the oxidation of phosphorus is a strongly exothermic reaction. The first step in the oxidation, $4P + 3O_2 = P_4O_6$, starts at a partial pressure of oxygen of approximately 570 mm at 20°. The heat of the reaction promptly raises the temperature of the P_4O_6, and because of this temperature increment the reaction, $P_4O_6 + 2O_2 = P_2O_5$ proceeds with the emission of light at 570 mm. From these considerations it

[1] Weiser and Garrison: Loc. cit.

[2] Abegg's Handbuch der anorganischen Chemie, 3, 421 (1907).

would follow that the film which protects phosphorus at its boundary pressure is P_2O_5.

The conclusions of Jungfleisch and of Scharff have been confirmed by L. and E. Bloch.[1] The latter investigators found that when air was blown over phosphorus under suitable conditions, the luminescence became elongated in the direction of the current; and with a sufficient increase in velocity of current, the luminescence separated itself from the phosphorus leaving a dark space. By suitably regulating the air current, the luminescence in the form of a column was removed several meters from the phosphorus. It was found that a condenser placed in or beyond the luminescence but not in the dark space became charged while an iodide-starch paper became blue in the regions in which the condenser was charged. From these results they concluded that luminescence, ionization, and ozone formation were produced not directly by the oxidation of phosphorus but by the oxidation of phosphorus trioxide. This conclusion was supported by the fact that if the dark space was cut suddenly, luminescent bubbles appeared which traveled slowly in opposite directions and finally disappeared. They explained this by assuming that the dark space contained P_4O_6 that inflamed spontaneously, the movement of the bubbles being the propagation of explosion waves.

Experimental

The luminescent reaction.—Although the evidence seems to indicate that the reaction $4P + 3O_2 = P_4O_6$, is not accompanied by luminescence, some additional experiments were carried out in an attempt to establish this point with certainty.

Experiment 1.—The experiment of L. and E. Bloch was repeated and their results confirmed. A piece of phosphorus was placed in one end of a tube twelve meters in length. By passing air through the tube a glow was obtained that extended the full length. If the air current was fast enough the

[1] Comptes rendus, 147, 842 (1908); Cf. Rinde: Ark. Kem. Min. Geol., 7, 21 (1917–18).

glow disappeared from the phosphorus entirely leaving a dark space. When this dark space was cut suddenly luminescence appeared spontaneously and traveled through the tube. These results indicate that the luminescence and the accompanying phenomena are due to the oxidation of phosphorus trioxide and that the first step $4P + 3O_2 = P_4O_6$ does not produce light. However, under the conditions of the experiment it was difficult to be sure that some phosphorus vapor was not carried along with the air stream and contributed to the glow. This suggested the following experiment:

Experiment 2.—Oxygen was passed through a tube containing phosphorus whose surface (15 sq cm) was freshly prepared by melting under water. At a temperature of 20° no light was obtained in the tube containing the phosphorus. When the oxygen passed over phosphorus was conducted into the air a faint, widely-distributed flame was obtained. If this oxygen be led through a tube heated above 70° at one point a cone-shaped flame was obtained in the heated region. In order to determine the temperature necessary to obtain a flame, the oxygen passed over phosphorus was led through a U-tube immersed in sulphuric acid, first heated to 100° and then allowed to cool slowly. The flame disappeared entirely between 75° and 65°. Since phosphorus glows in pure oxygen above 27° and since phosphorus trioxide does not glow in pure oxygen below 65°[1] it is almost certain that the combustible vapors contained in oxygen passed over phosphorus are trioxide and not phosphorus. The vapors are acidic, reddening neutral or alkaline methyl-red paper before they come in contact with the air.

That oxygen passed over phosphorus contains no phosphorus vapor was demonstrated as follows: The gas was conducted into an apparatus which consisted essentially of vessel C, Fig. 2. By means of the two-way stopcock, the gas was passed either directly into a tube heated to 75° or was first passed through 10 percent sodium hydroxide contained in C. A flame was obtained in the heated tube in the first

[1] Scharff: Loc. cit.

instance but disappeared when the gas was first passed through the alkali.

The experiments above described were repeated, substituting hydrogen for oxygen. Hydrogen was freed from all oxygen by passing first through three bottles of alkaline pyrogallol and then over warm phosphorus. It was next bubbled through warm alkali to remove oxide and finally over a second piece of phosphorus. In this way hydrogen containing phosphorus vapor but no oxides was obtained. When such a mixture was passed into the air through a tube 4 mm in diameter, a flame 1 cm long was obtained within the tube where the vapors met the air. Within this flame acids were produced which were readily detected by a strip of paper moistened with methyl red indicator. Back of the flame the vapors were neutral as one should expect. When the gas was passed through 10 percent alkali as above described the flame was not extinguished.

When oxygen is passed over phosphorus, phosphorus trioxide is formed without the emission of light. This trioxide burns spontaneously with a voluminous flame when exposed to the air. The oxide is absorbed by dilute alkali with the formation of Na_3PO_3 and NaH_2PO_3. When hydrogen is passed over phosphorus it contains phosphorus vapors which burn when exposed to the air with a small flame entirely different from the P_4O_6 flame. Moreover, unlike the trioxide, phosphorus vapor is not stopped by dilute alkali.

Summary.—The complete oxidation of phosphorus takes place in two steps, phosphorus trioxide being the intermediate product. The oxidation of phosphorus to phosphorus trioxide takes place without the emission of light; the oxidation of trioxide to pentoxide produces the characteristic phosphorus luminescence.

Ozone Formation

Although it has been known for a long time that ozone is formed during the oxidation of phosphorus, the nature of the chemical changes involved is still not definitely understood. Attention has been called earlier in this paper to the view of

van't Hoff[1] and of Baker[2] that phosphorus is attacked by oxygen only after the molecules have dissociated into positive and negative ions, one of which oxidizes the phosphorus while the other reacts with an oxygen molecule to form ozone or with some other substance capable of oxidation. This view is not shared by Schenck,[3] who believes that electrons are formed during the oxidation of phosphorus which convert oxygen into ozone. It is evident that the energy necessary for the formation of ozone must come from the reaction. The process is thus an example of the transformation of one form of chemical energy into another. According to Ostwald[4] such a transformation can result only by so-called coupled reactions. Ostwald assumes the primary reaction to be the formation of a hypothetical peroxide of phosphorus; and the secondary reaction to be the decomposition of this oxide to form ozone and phosphorous acid. In line with this view Schönbein[5] showed that both ozone and hydrogen peroxide are formed during the oxidation of phosphorus in the presence of moisture; whereas neither is formed in the absence of moisture. This observation was confirmed by Schmidt[6] and later by Russell.[7]

Thorpe and Tuttle[8] claim that no ozone is formed during the oxidation of phosphorus trioxide and Scharff[9] and Schenck[10] concur in this view. As pointed out in the preceding section, L. and E. Bloch[11] claim that ozone is formed during this reaction. Anderegg[12] calls attention to the fact that the ions formed during the oxidation of phosphorus can account for

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[1] Zeit phys. Chem., **16**, 411 (1895).
[2] Jour. Soc. Chem Ind, **24**, 481 (1905).
[3] Sitzungsber. Akad. Wiss., Berlin, 1904.
[4] Zeit. phys. Chem., **34**, 248 (1900)
[5] Pogg. Ann., **65**, 69 (1845).
[6] Jour. prakt Chem., **98**, 414 (1866).
[7] Jour. Chem. Soc., **96**, 63 (1905).
[8] Ibid., **57**, 650 (1890).
[9] Zeit. phys. Chem., **62**, 179 (1908).
[10] Abegg's Handbuch der anorganischen Chemie, (3) **3**, 421 (1907).
[11] Comptes rendus, **147**, 842 (1908).
[12] Jour. Am Chem Soc, **39**, 2586 (1917).

only a very small part of the ozone formed; and expresses the opinion that oxygen atoms which may or may not be charged, are necessary for ozone formation. For the formation of these oxygen atoms he suggests that the oxygen molecule, coming in contact with the lower oxide, uses up one atom before the other has time to combine with the substance being oxidized. Another atom from a second molecule completes the oxidation of the phosphorus.

From the number of opinions expressed in this brief survey, it is evident that we are not yet certain of the mechanism of the process whereby ozone is formed during the oxidation of phosphorus. The quantitative investigation of this problem is complicated by the number of factors involved. One of these seems to have been pretty generally overlooked—namely the effect of light. It is well known that ultraviolet light produces ozone under suitable conditions;[1] and Centnerszwer and Petrikaln[2] have found that the ultraviolet spectrum of the luminescence produced by slowly oxidizing phosphorus contains 14 sharp lines varying in wave length from 3339 to 3252 A. U. and a band at 3252 A. U., which is probably made up of lines.

Experimental

The effect of the light from glowing phosphorus on ozone formation.—In order to determine the effect of the ultraviolet light from glowing phosphorus on the formation of ozone, the following experiment was carried out:

Experiment 1.—A round plate of transparent quartz, 3 cm in diameter and 1 mm in thickness was made one side of a small gas-tight vessel by cementing it securely to a watch glass of approximately the same diameter. Before sealing, a piece of filter paper moistened with potassium iodide-starch solution was placed within the space between the quartz and the glass. A piece of phosphorus was allowed to oxidize very close to the quartz for twenty-four hours. A distinct blackening of the starch-iodide paper showed that ozone is formed

[1] Goldstein: Ber. deutsch. chem. Ges., 36, 3042 (1902).
[2] Zeit. phys. Chem., 80, 235 (1912).

by the action of the ultraviolet light from glowing phosphorus.

The formation of ozone during oxidation of phosphorus trioxide.—Since there is a difference of opinion as to whether ozone is formed during the oxidation of phosphorus trioxide, the following experiment was performed:

Experiment 2.—A small piece of redistilled phosphorus trioxide was placed in a glass tube 4 mm in diameter and close to it a strip of paper moistened with a potassium iodide-starch solution. When moist air was passed first over the trioxide and then over the paper, the latter darkened slightly after a short time. If left in the trioxide vapor, however, the darkening faded out due to the interaction of iodine with the oxide. This reaction between phosphorus trioxide and iodine probably accounts for the failure of Thorpe and Tuttle and of Scharff to detect ozone formation during the oxidation of phosphorus trioxide.

Summary.—The mechanism of the process whereby ozone is formed during the oxidation of phosphorus is not known with certainty. It has been demonstrated (1) that the oxidation of phosphorus trioxide results in ozone formation and (2) that ozone is formed by the ultraviolet light emitted during the oxidation of phosphorus.

Conclusions

(1) Gaseous ions are formed during the oxidation of phosphorus and account for the conductivity of phosphorized air. These ions furnish nuclei about which oxides and water vapor condense forming a charged cloud.

(2) The cloud arising from glowing phosphorus contains equal numbers of positive and negative particles providing the element is not charged.

(3) Ions are formed in the reaction zone and may be readily drawn out by an electric field against a current of air sufficiently rapid to remove oxide particles and ozone.

(4) The decomposition of ozone and the action of ultraviolet light are unimportant as sources of ions in phosphorized air.

(5) The luminescence of phosphorus is not altered appreciably by charging the element.

(6) Radiations of the nature of radium rays, which penetrate black paper and thin metal plates, are not formed during the oxidation of phosphorus.

(7) The darkening of a photographic plate protected from light in the region of glowing phosphorus is due to the action of the vapors of hydrogen peroxide and phosphorus trioxide.

(8) Ions are formed during the oxidation of phosphorus trioxide and render the surrounding atmosphere a conductor.

(9) No evidence was obtained of the formation of a phosphorus "emanation" by the action of moisture on phosphorus trioxide.

(10) The vapors of phosphorus trioxide diffuse readily and when admitted to an electrometer they diffuse throughout the instrument and condense on the insulation. On the addition of moisture the condensed vapors are converted to acid which causes a leak across the insulation that is easily mistaken for a gaseous leak due to ionization.

(11) The complete oxidation of phosphorus takes place in two steps; phosphorus trioxide being the intermediate product. The first step in the oxidation takes place without the emission of light. The luminescence of oxidizing phosphorus is due to the oxidation of phosphorus trioxide.

(12) Ozone is formed during the oxidation of phosphorus trioxide. The failure of certain investigators to detect ozone formation in this reaction is due, probably, to the action of trioxide vapors with the iodine liberated in the usual starch-iodide test.

(13) Ozone is formed by the ultraviolet light emitted by glowing phosphorus.

The phenomenon of intermittent luminescence and the so-called catalytic action of certain vapors on the oxidation of phosphorus will be considered in the next paper in this series.

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CONTRIBUTION TO THE STOICHIOMETRY OF ADSORPTION. II

ADSORPTION OF POTASSIUM AND BARIUM SALTS OF VARIOUS ANIONS

BY SVEN ODÉN AND E. W. LANGELIUS

In the preceding paper[1] only nitrates of various metals were subjected to adsorption investigations, and the adsorbed quantity was then found to increase slightly with the molecular weight of the cation.

In this paper we have, by means of the same interferometrical method, studied the adsorption of various potassium and barium salts by charcoal.

As the adsorption power of the charcoal varies slightly in the different bottles as furnished by Merck, we have, of course, used the same specimen in each series, but we have also determined the adsorption isotherm for the various specimens against KNO_3 as adsorbent.

The specimen used by Mr. Andersson in the previous paper is indicated as A, and the various "washed portions" of this charcoal are specified as A I, A II, A III, etc.

New specimens are indicated as B I, B II, B III, etc., each new bottle being denoted by letter and each purification-fraction by a Roman figure.

As to the method of measuring we refer to the foregoing paper. It should only be noted that the concentration of 0.20 mole per liter was seldom surpassed, so that there was no need to reckon with a variable μ for the concentration-value of the scale-unit, except in some special cases, as for instance, in Table 12.

CHAPTER 8

8. Adsorption of Potassium Salts by Charcoal

The measurements with about a dozen various potassium salts which were all purified by repeated crystallization from

[1] Jour. Phys. Chem., **25**, 311 (1921).

alcohol and water, are recorded in Tables 3–15, where the notations are generally the same as in the paper published together with H. Andersson. The adsorption curves are traced graphically in Figs. 5 and 6. If we first consider the various halogen salts, it appears clearly that, with anions of increasing

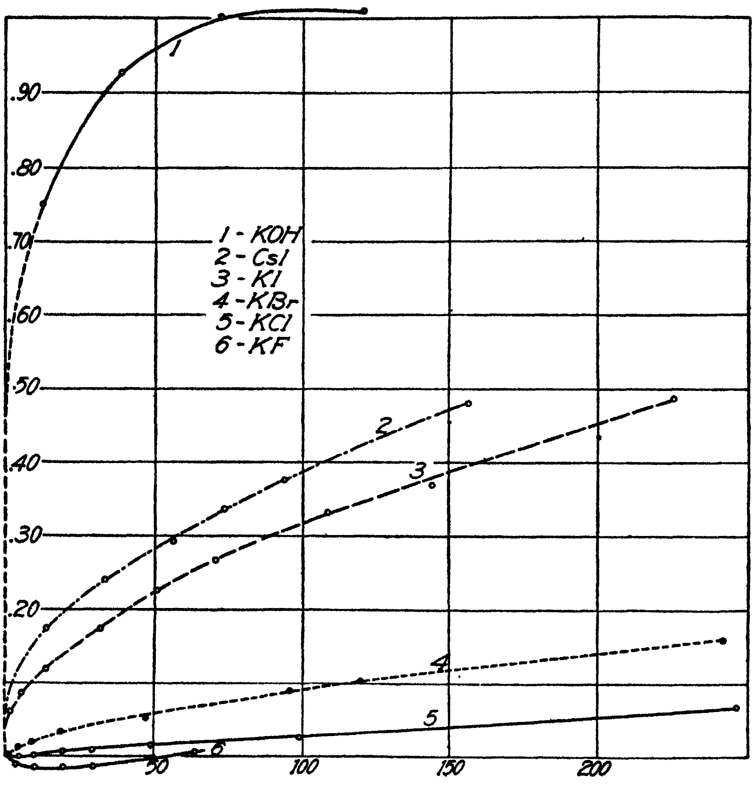

Fig. 5

atomic weight, a marked increase in the adsorbed quantity is obtained. The variation with the cation is, as demonstrated by the curves for the two iodides, by no means so considerable.

It is to be noticed that the adsorption of the fluorides was so small that no trustworthy values could be obtained (most of them gave negative values for the adsorbed quantity).

The observations agree tolerably well with the adsorption formula given by Freundlich, if not too wide intervals are considered. This is seen from the last columns of the tables, where the values calculated from the equation beneath every table, are compared with the observed quantity. The quantities K and β in this equation are obtained graphically by plotting log c against log y.

Again, if we note the values of the quantities K and β for the groups of the halogen salts, including the radical (SCN), we find that the K-values increase from $0.314.10^{-3}$ for the chloride, to $29.5.10^{-3}$ for the iodide; whereas the β-values show a marked decrease from 0.98 to 0.51.

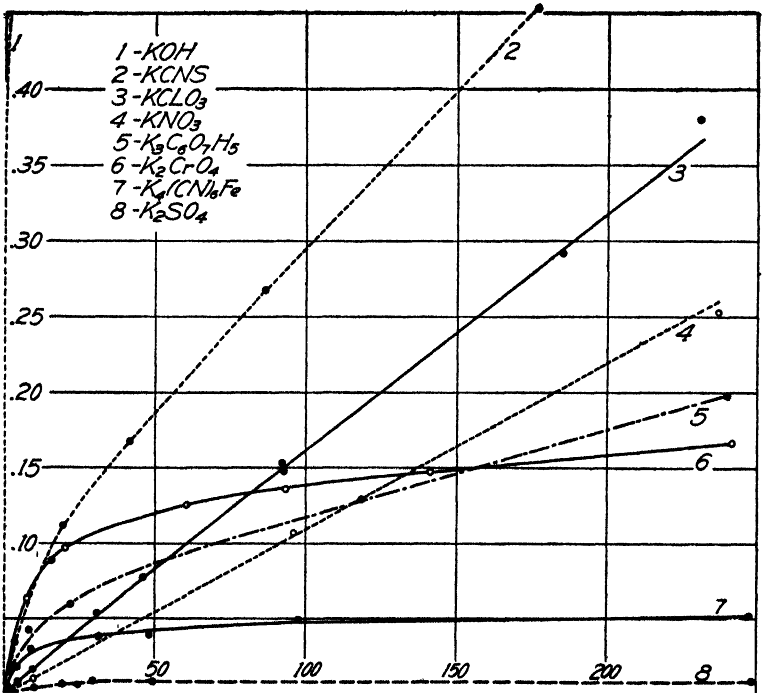

Fig. 6

TABLE 1

Salt adsorbed	Mol. weight of the anion	K	β
CsI	127	45.7×10^{-3}	0.46
KI	127	29.5×10^{-3}	0.51
NaI	127	$(50.5) \times 10^{-3}$	(0.41)
KSCN	58	15.41×10^{-3}	0.66
KBr	80	4.22×10^{-3}	0.66
KSO_3	—	—	—
KCl	35.5	0.314×10^{-3}	0.98
KF	19	(0.139×10^{-7})	(3.25)[1]

[1] Adsorption hardly measurable.

Considering the curves in Fig. 6, representing the adsorption-isotherms of other potassium salts investigated, the most striking feature is that the curves in several cases cross each other. This signifies, of course, that the order of adsorption varies with the concentration.

Thus at $c = 0.010$ mole, the order of the adsorbed quantity varies with the anion in the following order

$$F' < Cl' < SO_4'' < NO_3' < ClO_3' < Br' < Fe(CN)_6'''' < (\text{citrate})''' < SCN' < CrO_4'''' < I'$$

at 0.05 mole the order is:

$$F' < SO_4'' < Cl' < Fe(CN)_6'''' < Br' < NO_3' < (\text{citrate})''' < ClO_3' < CrO_4'' < SCN' < I'$$

whereas at 0.2 mole (we have)

$$< SO_4'' < F' < Fe(CN)_6'''' < Cl' < Br' < CrO_4'' < (\text{citrate})''' < NO_3' < ClO_3' < I' < CN',$$

It thus appears that for increasing value of c the salts of the polyvalent ions are displaced in the direction of less adsorption.

The shape of the adsorption isotherms for polyvalent ions is also different, these ions having small exponents, so that, after an interval of marked curvature, the increase in the adsorbed quantity for increasing c is but small; the factor c^β tending towards unity. For the sulphate this nearly constant value is attained at a concentration of 0.1 mole, and

TABLE 2

Salt adsorbed	Valency of the anion	$1/\beta$	K_α	α
$K_4Fe(CN)_6$	4	5.25	19.4×10^{-3}	0.19
K_3-(citrate)	3	2.00	12.4×10^{-3}	0.50
K_2CrO_4	2	4.76	51.4×10^{-3}	0 21
K_2SO_4	does not follow the exponential law			
$KClO_3$	1	1.03	1.86×10^{-3}	0.97
KNO_3	1	1.10	1.70×10^{-3}	0.91
KSCN	1	1.52	15.4×10^{-3}	0.66
KOH	1	?	?	—

the isotherm does not agree at all with the Freundlich formula. No specific relation is to be found between the valency and the coefficients K and α, as is clearly seen from Table 2. On the whole, the group of curves represented in Fig. 2 imparts the conviction that no formulae whatever give an adequate representation of the adsorption process.

In the following tables:

b is the concentration of the salt solution (B) before adsorption, expressed in millimoles per 1000 ccm (cc).

$\mu_{1/2}$, μ_1 and μ_4 are the concentration values of each scale-unit, expressed in millimoles per 1000 ccm, according to whether the 0.5 cm compartment or the 1 or the 4 cm was employed.

α is the interferometrical difference in scale-units between the solution before, (B), and after adsorption, (A), with m (1.25) gram per v (25) ccm.

Thus $y = \dfrac{\alpha\mu . v}{1000. m}$ is the quantity adsorbed by 1 gram charcoal from 20 ccm solution, expressed in millimoles.

$c = b - \alpha\mu$ is the concentration of the solution after adsorption also expressed in millimoles per 1000 ccm.

log y and log c are the Briggsian logarithms.

Finally:

y' (calc.) contains the values for the adsorbed quantity as calculated by means of the Freundlich formula $y = Kc^\beta$.

TABLE 3

Adsorption of CsI by Charcoal A IV

$\mu_1 = 0.101$; $m = 1.25$ g; $v = 25$ ccm

No.	b	α	y	log y	c	log c	y (calc.)
1	180.8	+238	0.481	0.682–1	156.8	2.195	0.481
2	90.4	+167	0.337	0.527–1	73.6	1.887	0.339
3	45.2	+119	0.240	0.380–1	33.2	1.521	0.233
4	22.6	+ 86	0.174	0.240–1	13.9	1.143	0.155
5	71.0	+144	0.293	0.467–1	56.4	1.751	0.297
6	112.5	+187	0.378	0.578–1	93.6	1.971	0.378

The values in the last column are calculated by means of the equation

$$y = 0.0457\ c^{0.465}$$

TABLE 4

Adsorption of KI by Charcoal A IV

$\mu_1 = 0.054$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc.)
1	62.5	+209	0.226	0.354–1	51.2	1.709	0.222
2	125.0	+309	0.335	0.525–1	108.3	2.035	0.323
3	250.0	+452	0.489	0.689–1	225.6	2.353	0.475
4	40.8	+161	0.174	0.240–1	32.1	1.507	0.175
5	163.3	+343	0.371	0.570–1	144.8	2.161	0.378
6	83.3	+248	0.268	0.429–1	70.3	1.847	0.257
7	20.0	+109	0.118	0.072–1	14.1	1.149	0.137
8	10.0	+ 80	0.086	0.937–2	5.7	0.756	0.095
9	5.0	+ 56	0.061	0.782–2	2.0	0.301	0.062
10	1.0	+ 5	0.005	0.724–3	0.7	0.845–1	0.042

The values of the last column are calculated by means of the equation

$$y = 0.0295\ c^{0.513}$$

TABLE 5

Adsorption of NaI by Charcoal A IV

$\mu_1 = 0.1144$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc.)
1	25	+ 76	0.174	0.240–1	16.3	1.212	0.159
2	75	+119	0.272	0.435–1	61.4	1.788	0.272
3	125	+150	0.344	0.537–1	107.8	2.033	0.344
4	250	+207	0.474	0.676–1	226.3	2.355	0.466
5	100	+135	0.310	0 490–1	84.6	1.927	0.312
6	125	+148	0.339	0.530–1	108.0	2.033	0.344
7	200	+182	0.417	0.620–1	179.2	2.253	0.423

The values in the last column are calculated by means of the equation

$$y = 0.0505\ c^{0.410}$$

TABLE 6

Adsorption of KBr by Charcoal A IV

$\mu_1 = 0.0910$; $m = 1.25$ g; $v = 25$ cc

No	b	α	y	log y	c	log c	y' (calc.)
1	1	− 1	−0.0018	—	0.9	—	—
2	5	+ 6	+0.0109	0.038–2	4.5	0.650	0.0113
3	10	+10	+0.0182	0.260–2	9.1	0.960	0.0182
4	20	+18	+0.0328	0.516–2	18.4	1.275	0.0290
5	50	+29	+0.0529	0.723–2	47.4	1.676	0.0545
6	100	+50	+0.0910	0.960–2	95.5	1.980	0.0865
7	125	+57	+0.103	0.013–1	119.9	2.079	0.101
8	250	+88	+0.160	0.204–1	242.0	2.384	0.160

The values in the last column are calculated by means of the equation

$$y = 0.00422\ c^{0.662}$$

TABLE 7

Adsorption of KCl by Charcoal A IV

$\mu_1 = 0.1335$; $\mu_4 = 0.0334$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc.)
1	5	(α_1 =) — 1	—0.00200	—	5.1	—	—
2	10	(α_1 =) + 1	+0.0007	—	9.97	—	—
3	20	(α_1 =) + 9	+0.0060	0.778–2	19.7	1.294	0.0058
4	30	(α_1 =) +12	+0.0080	0.903–2	29.6	1.471	0.0086
5	50	(α_1 =) +24	+0.0160	0.204–2	49.2	1.692	0.0143
6	100	(α_4 =) +10	+0.0267	0.427–2	98.7	1.994	0.0282
7	250	(α_4 =) +26	+0.0695	0.842–2	246.5	2.392	0.0694

The values of the last column are calculated by means of the equation

$$y = 0.000314\, c^{0.98}$$

TABLE 8

Adsorption of KF by Charcoal A IV

$\mu_4 = 0.2457$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	c
1	5	—13	—0.0160	5.8
2	10	—16	—0.0197	11.0
3	20	—15	—0.0185	20.9
4	30	—15	—0.0185	30.9
5	50	—10	—0.0123	50.6
6	60.7	+ 4	+0.0049	60.4

TABLE 9

Adsorption of KSCN by Charcoal A IV

$\mu = 0.0728$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc.)
1	5	+ 24	0.035	0.544–2	3.25	0.512	0.034
2	10	+ 50	0.043	0.634–2	7.85	0.895	0.060
3	20	+ 61	0.089	0.950–2	15.5	1.190	0.093
4	50	+115	0.168	0.225–1	41.6	1.619	0.178
5	100	+184	0.268	0.428–1	86.6	1.938	0.288
6	25	+ 77	0.112	0.050–1	19.4	1.288	0.108
7	200	+311	0.453	0.656–1	177.1	2.248	0.465
8	250	+388	0.565	0.752–1	221.7	2.346	0.540

The values in the last column are calculated by means of the equation

$$y = 0.0154\, c^{0.658}$$

TABLE 10

Adsorption of $KClO_3$ by Charcoal A IV

$\mu = 0.1351; m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc.)
1	5	+ 3	0.0081	0.909–3	4.6	0.663	0.0083
2	10	+ 6	0.0162	0.210–2	9.2	0.964	0.0163
3	33.5	+ 20	0.0540	0.732–2	30.6	1.486	0.0525
4	50	+ 29	0.0783	0.894–2	46.1	1.664	0.0782
5a	100	+ 57	0.1539	0.187–1	92.3	1.965	0.154
5b	100	+ 55	0.1485	0.172–1	92.6	1.967	0.154
6	200	+108	0.292	0.465–1	185.4	2.268	0.303
7	250	+141	0.380	0.580–1	231.0	2.364	0.379

The values in the last column are calculated by means of the equation

$$y = 0.00186\, c^{0.975}$$

TABLE 11

Adsorption of Potassium Citrate by Charcoal A IV

$\mu = 0.03; m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc)
1	25	99	0.060	0.778–2	22.0	1.342	0.0586
2	125	217	0.130	0.114–1	118.5	2.074	0.135
3	250	332	0.199	0.299–1	240.0	2.380	0.193

The values in the last column are calculated by means of the equation

$$y = 0.0124\, c^{0.500}$$

TABLE 12

Adsorption of KNO_3 by Charcoal A IV

$\mu_0 = 0.147; m = 1.25$ g; $v = 25$ cc

On account of the greater concentration in this table we have employed the vaiiable μ-value

$$\mu = \mu_0(1 + \gamma c) \text{ where } \gamma = 0.00027$$

No.	b	α	y	log y	c	log c	y' (calc.)
1	10	+ 4	0.0119	0.070–2	9.4	0.973	0.013
2	100	+ 36	0.108	0.034–1	94.6	1.975	0.109
3	250	+ 82	0.253	0.329–1	237.4	2.375	0.255
4	500	+145	0.470	0.672–1	476.5	2.677	0.474

The values in the last column are calculated by means of the equation

$$y = 0.00170\, c^{0.915}$$

TABLE 13

Adsorption of K_2CrO_4 by Charcoal A IV

$\mu = 0.0545$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	$\log y$	c	$\log c$	y' (calc.)
1	10	+ 68	0.074	0.869–2	6.3	0.799	0.0745
2	66.7	+116	0.126	0.100–1	60.4	1.781	0.123
3	100	+126	0.137	0.137–1	93.2	1.969	0.135
4	25	+ 89	0.097	0.986–2	20.2	1.305	0.0966
5	150	+136	0.148	0.170–1	142.6	2.154	0.148
6	250	+153	0.167	0.222–1	241.7	2.383	0.165

The values in the last column are calculated by means of the equation

$$y = 0.0514\, c^{0.213}$$

TABLE 14

Adsorption of $K_4Fe(CN)_6$ by Charcoal A IV

$\mu = 0.018$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	$\log y$	c	$\log c$	y (calc.)
1	1	+ 10	0.004	—	0.8	—	—
2	5	+ 51	0.018	0.255–2	4.1	0.613	0.0255
3	10	+ 82	0.030	0.477–2	8.5	0.929	0.0290
4	33.3	+102	0.037	0.568–2	31.5	1.498	0.0375
5	50	+108	0.039	0.591–2	48.0	1.681	0.0405
6	100	+136	0.049	0.690–2	97.5	1.989	0.0465
7	250	+148	0.053	0.724–2	247.4	2.393	0.0550

The values in the last column are calculated by means of the equation

$$y = 0.0194\, c^{0.190}$$

TABLE 15

Adsorption of K_2SO_4 by Charcoal A IV

$\mu_1 = 0.0632$; $\mu_4 = 0.0158$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	c
1	25	($\alpha_4 =$) +19	0.0060	24.7
2	10	($\alpha_4 =$) +12	0.0038	9.8
3	20	($\alpha_4 =$) +21	0.0066	19.7
4	30	($\alpha_4 =$) +28	0.0088	29.6
5	50	($\alpha_4 =$) +25	0.0080	49.6
6	100	($\alpha_4 =$) +28	0.0088	99.6
7	250	($\alpha_1 =$) + 8	0.0101	249.5

TABLE 16

Adsorption of KOH by Charcoal A V

$m = 1.25$ g; $v = 25$ ccm

For this substance b and c were determined by titration.

$$y = \frac{(b - c)\,v}{1000\,m}$$

No.	b	c	$b-c$	y
1	173	120	53	1.06
2	123	72	51	1.02
3	85	38.8	46.2	0.925
4	50	12.5	37.5	0.75

CHAPTER 9
Adsorption of Barium Salts by Charcoal

Experiments similarly executed with several barium salts are recorded in Tables 18–23, and graphically in Fig. 7.

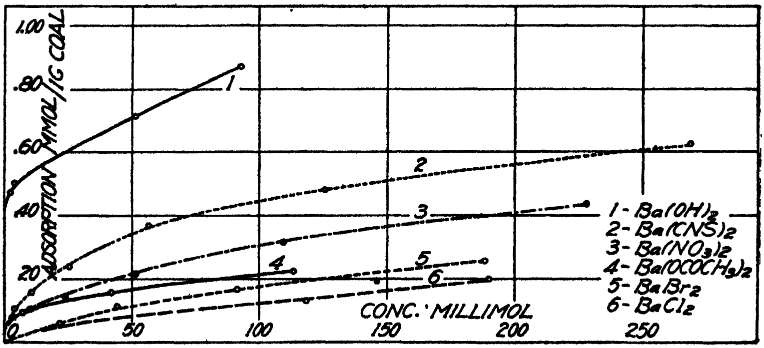

Fig. 7

These curves—except perhaps for the acetate—do not cross each other like the potassium curves, and at 0.05 mole concentration the order of adsorption is:

$$Cl' < Br' < (Ac)' < NO_3' < SCN' < OH'$$

Thus the order is the same as for potassium salts at the same concentration.

We could not find any barium salts with polyvalent ions adapted to similar measurements, because either small sol-

ubility or great hydrolysis complicate the phenomena; as exemplified by the citrate or the phosphates.

Noting the values of K and β we find the β-values astonishingly near 0.48 for all salts, so that the adsorption mainly depends on the coefficient which increases from 13×10^{-3} for the chloride to 0.4 for the hydroxide.

TABLE 17

Salt adsorbed	Mol. weight of the anion	K	β
$Ba(OH)_2$	34	—	—
$Ba(OCOCH_3)_2$	118	50.7×10^{-3}	0.31
$Ba(SCN)_2$	116	53.0×10^{-3}	0.47
$Ba(NO_3)_2$	124	32.3×10^{-3}	0.48
—	—	—	—
$BaBr_2$	160	18.5×10^{-3}	0.48
$BaCl_2$	71	13.0×10^{-3}	0.47

The group of curves in Fig. 7 thus nearly represents what by W. Mecklenburg is called "affine adsorption-isotherms" where the value of any curve may be obtained from any other by multiplication of the y-values by a definite constant.

TABLE 18

Adsorption of $Ba(OH)_2$ by Charcoal A V

$m = 1.25$ g; $v = 25$ ccm

For this substance b and c were determined by titration:

$$y = \frac{(b - c)\, v}{1000\, m}$$

No.	b	c	$b-c$	y
1	136.5	93.0	43.5	0.87
2	87.0	51.5	35.5	0.71
3	28.0	2.0	26.0	0.52
4	25.0	1.3	23.5	0.47

TABLE 19

Adsorption of $Ba(CNS)_2$ by Charcoal A V

$\mu_{1/2}\ \mu_{1/2} = 0.0572$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y (calc)
1	9.35	+ 93	0.106	0.026–1	4.05	0.607	0 102
2	18.75	+137	0.156	0.193–1	10.95	1 039	0.162
3	37.50	+207	0.236	0.373–1	25.70	1.410	0 242
4	75.00	+320	0.365	0.562–1	56.75	1.754	0.351
5	150.00	+423	0.481	0.683–1	126.0	2.100	0 508
6	300.00	+550	0.627	0.797–1	268.7	2.429	0.730
7	6.55	+ 84	0 0958	0.981–2	1.76	0.246	0.069
8	28.35	+186	0.212	0.326–1	17.75	1.249	0.204
9	100.00	+373	0.425	0.628–1	78.8	1.897	0.408

The values in the last column are calculated by means of the equation

$$y = 0.0530\ c^{0\ 468}$$

TABLE 20

Adsorption of $Ba(NO_3)_2$ by Charcoal A V

$\mu_{1/2} = 0.089$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y (calc.)
1	7.3	+ 45	0.081	0.908–2	3.25	0.512	0.057
2	14.6	+ 60	0.107	0.029–1	9.25	0.966	0.094
3	31.25	+ 82	0.145	0.161–1	24.00	1.380	0.149
4	62.5	+122	0.217	0.336–1	51.65	1.713	0.215
5	125 00	+178	0.315	0.498 1	109 3	2.038	0 308
6	250.00	+247	0.439	0.642–1	228.0	2.358	0.438

The values in the last column are calculated by means of the equation

$$y = 0.0323\ c^{0\ 480}$$

TABLE 21

Adsorption of $BaBr_2$ by Charcoal A V

$\mu_{1/2} = 0\ 065$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y (calc)
1	50	+ 89	0.115	0.061–1	44.25	1.464	0.116
2	100	+126	0.164	0.215–1	91.8	1.963	0.164
3	200	+176	0.232	0.365–1	188.4	2.275	0.231

The values in the last column are calculated by means of the equation

$$y = 0.0185\ c^{0\ 482}$$

TABLE 22
Adsorption of $Ba(OCOCH_3)_2$ by Charcoal A V
$\mu_{1/2} = 0.0815$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y (calc.)
1	12	+ 59	0.097	0.987–2	7.2	0.857	0.093
2	50	+ 95	0.156	0.193–1	42.2	1.625	0.160
3	125	+136	0.223	0.348–1	113.8	2.056	0.218

The values in the last column are calculated by means of the equation

$$y = 0.0507\ c^{0.308}$$

TABLE 23
Adsorption of $BaCl_2$ with Charcoal A V
$\mu_{1/2} = 0.045$; $m = 1.25$ g; $v = 25$ cc

No.	b	α	y	log y	c	log c	y' (calc.)
1	7.8	+ 68	0.061	0.785–2	4.8	0.680	—
2	15.6	+ 78	0.070	0.845–2	12.1	1.083	0.042
3	31.25	+ 90	0.081	0.908–2	27.2	1.435	0.061
4	62.5	+107	0.096	0.982–2	57.7	1.761	0.087
5	125.00	+135	0.121	0.083–1	119.0	2.075	0.121
6	250.00	+188	0.168	0.225–1	241.6	2.383	0.169

By means of the last two values (log y, log c), Nos. 5 and 6, the equation

$$y = 0.0130\ c^{0.467}\ \text{is obtained.}$$

ADSORPTION BY PRECIPITATES IV

BY HARRY B. WEISER

"Acclimatization"

It is an interesting fact that the amount of electrolyte necessary to coagulate a colloid completely is influenced by the rate at which the electrolyte is added. Since a quantity that will cause complete coagulation when the addition is rapid will not cause complete coagulation when the addition is slow, the colloid is said to become "acclimatized" to the presence of electrolyte and the phenomenon is called "acclimatization."[1]

Historical

Several cases of "acclimatization" of colloids are referred to in the literature. Freundlich[2] observed this phenomenon first with colloidal arsenious sulphide: "In the course of the precipitation experiments described above, it was observed accidentally that, among other things, the rate with which the salt solution was added to the colloid had considerable influence on the precipitation value. This led to the conclusion that the precipitation process is not static but involves the element of time. In view of the investigations of Nernst who showed, for example, that marked differences in potential arise by the diffusion of ions, one might expect that diminution of the surface, that is precipitation, could result from the same cause. To test these points a series of experiments was carried out.

"The first experiment was as follows: The amount of barium chloride solution containing 9.55 millimoles of $BaCl_2$ per liter, necessary to precipitate completely in two hours an arsenious sulphide colloid containing 5.752 millimoles of As_2S_3 per liter, was first determined according to the method previously described. The same amount of electrolyte, 2 cc, was next added dropwise to the same amount of colloid, 20 cc, in 18

[1] Taylor: The Chemistry of Colloids, 98, 310 (1915).

[2] Zeit. phys. Chem., **44**, 143 (1903).

hours, 27 days and 45 days, respectively. After the addition of each drop the solution was shaken once. Two hours after the addition of the last drop the solutions were filtered and it was found that the filtrate was still quite cloudy—the cloudiest solution being the one to which the electrolyte was added slowest. In order to precipitate the remainder of the first solution completely, 1.5 cc of the same barium chloride solution was added; and after two hours it was clear. Likewise to the remainder of the second solution was added 1 cc and to the third 2 cc of electrolyte. Complete precipitation was observed in the second after two days and in the third after two hours. Nearly the same amount was required as if no slow addition had been made.

"These observations cannot be explained by assuming that they arise from the distribution equilibrium of the ions or on equilibrium conditions generally, since these depend solely on the concentration and the latter is as great after rapid addition as after slow, considering that the flocks resulting gradually by slow addition adsorb only a very small amount. On the other hand a process like diffusion which requires time undergoes a real change according as the addition is rapid or dropwise. In the first case a large difference in concentration is produced which causes a marked diffusion; in the second case the difference in concentration is kept so small that only inappreciable diffusion processes can go on. The latter case cannot be realized entirely, since at the point at which the drop enters the solution appreciable concentration differences are always present.

"A second deduction tested was whether small additions of salt which produce practically no diffusion will cause no distinct action on the colloid in the course of a long time. For this purpose 100 cc portions of colloidal arsenious sulphide were placed in each of three Jena glass flasks which were closed carefully after first adding 100 cc of pure water or a like volume of potassium chloride solutions of different concentrations. After 340 days all these solutions possessed the same reddish yellow color as the freshly prepared colloid;

and there had separated only a fine scum and a few flocks of arsenious sulphide. All these were filtered and the content again determined. The results are given in the following table:

	I	II	III
KCl millimoles per liter	0	1.219	2.438
As_2S_3 millimoles per liter (original solution)	11.272	11.272	11.272
As_2S_3 millimoles per liter (after 340 days)	9 570	9.603	9.453

"It is evident that the addition of 1.219 millimoles of potassium chloride per liter has practically no influence, while the addition of 2.438 millimoles per liter has a very slight influence. These numbers lose some of their value on account of the fact that only the smallest part of the decrease in As_2S_3 content can be attributed to coagulation, the greater part being due to the decomposition into H_3AsO_3 and H_2S. Still, I believe that a certain amount of importance can be attached to the above values since a solution which contained 3.9 millimoles of potassium chloride per liter under the same conditions was as good as completely coagulated in the same time; the supernatant liquid had a faint yellow color and therefore contained but an unweighable amount of As_2S_3."

Similar experiments were carried out by Freundlich[1] on colloidal hydrous ferric oxide: "To 20 cc of a colloid containing 20.45 millimoles of $Fe(OH)_3$ per liter was added 2 cc of magnesium sulphate solution containing 4.82 millimoles per liter. The addition was made dropwise in the course of eight days; after each addition the flask was shaken once. Although a salt solution of this concentration precipitated the colloid completely after two hours, by this slow addition the solution was not entirely clear two hours after the last drop was added; and the filtrate still contained ferric hydroxide. The addition of three drops more (0.13 cc) of magnesium sulphate solution was sufficient to coagulate the remainder within an hour."

[1] Zeit. phys. Chem., **44**, 151 (1903).

Observations similar to the above were made by Freundlich[1] with colloidal platinum and by Höber and Gordon[2] with albumin. A similar behavior which is known as the Danysz effect, is observed in the toxin-antitoxin reaction.[3] Thus when a diphtheria toxin is treated with its antitoxin, the reduction in toxicity depends on the manner in which it is added, that is, an amount of antitoxin which is exactly sufficient to neutralize a given amount of toxin when added all at once is not nearly sufficient to neutralize the same amount of toxin when added little by little, with moderate intervals between each addition. This similarity between the Danysz effect and true colloidal precipitation suggests that certain toxins and antitoxins are colloidal in nature.

Theoretical

As pointed out in the preceding section Freundlich suggests that the so-called "acclimatization" phenomenon may be due to difference in diffusion through the electrical film or layer which protects the particles. He argues that if the amount necessary to cause precipitation is added all at once, there is such a marked change in concentration that a marked diffusion through the colloid-liquid interface takes place; whereas, if the electrolyte is added very slowly there is no marked change in concentration at any instant and so the diffusion is inappreciable. It would seem that this explanation does not account for the fact that an amount of electrolyte added all at once, which will cause complete precipitation in two hours, say, will not cause complete precipitation in two hours after the same concentration is reached by slow addition. Later in discussing the cause of this phenomenon, Freundlich[4] suggests that the difference in the effect of rapid and slow addition of an electrolyte to a colloid is traceable to the difference in the disturbance produced in the solution.

[1] Zeit. phys. Chem., **44**, 153 (1903).
[2] Beitr. chem. Physiol. Path., **5**, 436 (1904).
[3] See Taylor: The Chemistry of Colloids, 310 (1915).
[4] Kapillarchemie, 348 (1910).

"The discharge of the colloidal particles and the asymmetry, 'the disturbance,' resulting therefrom, vary with the nature, rapidity, etc., of the electrolyte additions. Hence, it has been found to be extremely difficult to obtain the same precipitation value under apparently identical conditions. The matter of the small disturbances which carry the colloid through all possible degrees of stability by slow addition of electrolyte naturally does not have the same effect as the rapid discharge and the rapid exceeding of the threshold value and growth of flocks resulting therefrom."

Freundlich's suggestions can scarcely be regarded as an explanation of the effect on the precipitation value of the rate of addition of electrolyte. Since a colloid stabilized by preferential adsorption of ions of a given charge is coagulated completely only after neutralization of the particles by adsorption of an equivalent amount of ions of opposite charge, it would seem that the rate of addition must have an effect on the adsorption which in turn determines the precipitation value. Approaching the matter from this point of view, we arrive at an explanation that is capable of experimental verification:

In previous communications[1] it has been pointed out that the adsorption of equivalent amounts of all the precipitating ions will effect neutralization of the charge on the particles of a given amount of colloid providing the stabilizing influence of the added ion having the same charge as the colloid is kept constant. Since the adsorption of a given ion depends on the concentration, it is usually, if not always, necessary to add to the colloid more of the precipitating ion than would be necessary to effect neutralization if all were adsorbed. The excess is then adsorbed wholly or in part by the electrically neutral particles. The actual amount of an ion carried down by a precipitated colloid is therefore determined (*a*) by the adsorption of the electrically charged particles during neutralization and (*b*) by the adsorption of the electrically neutral particles during the process of agglomera-

[1] Weiser and Middleton: Jour. Phys. Chem., **24**, 30, 630 (1920).

tion and settling. The amounts of (*a*) are equivalent, but the amounts of (*b*) which have been pretty generally overlooked, vary with the nature and concentration of the ion concerned. Viewing the matter in this way, the precipitation value obtained by adding the electrolyte all at once is such a concentration of precipitating ion that sufficient adsorption to cause neutralization can result in a definite time. If this amount of electrolyte is added very slowly, there results a gradual increase in the size of the particles due to partial neutralization by adsorption. After the addition of enough electrolyte, partial agglomeration takes place. These coagulated particles have adsorbed not only enough ions to effect their complete neutralization; but the neutralized particles have carried down an additional amount during agglomeration. This adsorption by electrically neutral particles during the fractional precipitation accompanying slow addition of electrolyte, causes such a decrease in the ionic concentration that a greater amount must be added to effect complete neutralization by this fractional process. Rapid addition furnishes all at once the critical concentration of precipitating ion necessary for neutralization by adsorption. To obtain the same results by the very slow process, more electrolyte must be added to compensate for the loss of precipitating ion adsorbed by the electrically neutral particles that separate gradually during the process.

As above described, Freundlich has shown that the stability of colloidal arsenious sulphide is affected but slightly by a concentration of ion far below the precipitation value. This is due to the fact that complete precipitation cannot take place below the concentration of ion necessary for complete neutralization by adsorption.

Experimental

The theory set down in the preceding section emphasizes the importance of adsorption during agglomeration for explaining the so-called "acclimatization" phenomenon. Before taking up the work on adsorption an account will be given of

some experiments carried out in order to become acquainted with the effect of rate of addition of electrolyte on the precipitation value.

Precipitation Experiments

Experiments with Hydrous Ferric Oxide.—Colloidal hydrous ferric oxide was prepared by the method described in detail in a recent communication.[1] The approximate precipitation value for potassium oxalate was determined by titrating 10 cc of the colloid with $N/50$ $K_2C_2O_4$, using a 2 cc Ostwald pipette calibrated in tenths of a cubic centimeter. Knowing the approximate precipitation value, a series of experiments was carried out in which measured amounts of electrolyte were added all at once to 20 cc of colloid, employing a slightly modified form of the mixing apparatus which was found so useful in previous investigations.[2] The precipitation value on slow addition was determined as follows: Twenty cubic centimeters of colloid were measured into a pyrex flask supplied with a rubber stopper. This stopper contained a 2 cc Ostwald pipette to the upper end of which was sealed a stopcock for convenience in retaining the solution in the small pipette and in making the small additions of electrolyte. The latter was added in 0.1 cc portions every hour for 10 hours, after which the solution was allowed to stand over night and the additions completed the next day. After each addition the flask was shaken once to ensure mixing. Approximately 30 hours elapsed between the addition of the first portion of the electrolyte and the conclusion of the experiment. The results confirm those of Freundlich. Whereas 1.8 cc of $N/50$ $K_2C_2O_4$ was sufficient to cause complete precipitation in 1 hour when added all at once, the precipitation was not complete one hour after the addition of the same amount of electrolyte by the slow method. By adding 0.1 cc more and allowing the solution to stand for an hour, a filtrate free from colloidal oxide was obtained. Three parallel experiments gave the same results.

[1] Weiser: Jour. Phys. Chem., **24**, 277 (1920).
[2] Weiser and Middleton: Loc. cit.

In connection with these experiments it was of interest to note that no precipitation of the colloid took place until very near the precipitation value. In other words, the precipitation value was fairly sharp even when thirty hours was taken for the addition of electrolyte. Since but few ions were removed by adsorption by neutralized particles until very near the precipitation concentration, one should expect but little variation in precipitation with rate of addition of electrolyte. This view is confirmed by our own experiments and those of Freundlich.

Experiments with Colloidal Arsenious Sulphide.—Colloidal arsenious sulphide was prepared by the method of Linder and Picton,[1] which consists essentially of passing hydrogen sulphide into a dilute solution of arsenious sulphide until no further action takes place, removing the excess hydrogen sulphide with a current of hydrogen. The experiments described above were repeated with this colloid. In order to determine when coagulation was complete the solution after filtration, was examined in small Nessler tubes. Even a trace of colloidal sulphide was detectible in this way. Precipitation values were determined for strontium chloride and potassium chloride. On rapid addition, 2.05 cc of $N/50$ strontium chloride and 2.50 cc of $N/2$ potassium chloride were necessary to precipitate completely 20 cc of colloid. The slow addition of the electrolyte in 0.1 cc portions over a period of approximately 36 hours required 2.50 cc of strontium chloride and 2.70 cc of potassium chloride solutions.

Unlike colloidal hydrous ferric oxide, colloidal arsenious sulphide started to precipitate after the addition of a few tenths of a cubic centimeter of electrolyte and the fractional precipitation continued until coagulation was complete. These are the exact conditions which would tend to make a distinct difference between the precipitation values on rapid and slow addition. The results show this to be the case. The variations are not so marked as observed by Freundlich, but it is not known what procedure was followed by Freundlich to

[1] Jour. Chem. Soc., 61, 137 (1892).

determine just how much electrolyte must be added all at once after the initial titration in order to obtain complete coagulation. A source of error suggests itself: Freundlich may have used an old colloid, and it is well known that colloidal As_2S_3 decomposes on standing to give arsenious acid and hydrogen sulphide. Barium ions added very slowly to such a solution would be removed in part as insoluble barium arsenite before the concentration was sufficiently high for marked adsorption by the colloid.

Experiments on Adsorption

As I have pointed out, it is usually considered that equivalent amounts of various ions are adsorbed by a precipitated colloid at the precipitation concentration. This conclusion is deduced from the fact that the adsorption of equivalent amounts of various ions will produce neutralization; but fails to take into account the adsorption of the neutralized particles during agglomeration. In order to get some idea of the magnitude of the adsorption of neutralized particles a series of experiments was carried out in which the adsorption of various ions by precipitated hydrous ferric oxide was determined at and above the precipitation concentration. The colloid employed contained 1.824 grams of Fe_2O_3 per liter. The method of procedure was as follows: The precipitation value of the ion under consideration was first determined in the usual way, after which a quantity of electrolyte of known concentration was added all at once to 125 cc of colloid contained in a 200 cc wide-mouth bottle. The solution was allowed to stand for an hour after which it was centrifuged for 20 minutes at 3000 r. p. m. By this process the precipitated oxide was matted firmly in the bottom of the container so that the supernatant liquid could be removed quantitatively and the vessel thoroughly rinsed. It was intended to wash the precipitate by shaking with distilled water and repeating the centrifuging as was done in previous experiments.[1] This was found to be impossible even with divalent ions since at

[1] Weiser and Middleton: Loc. cit.

concentrations so near the precipitation value, immediate washing resulted in slight peptization. However, since the solutions were quite dilute, the amounts remaining in the small space occupied by the precipitated oxide were very slight. Moreover, absolute adsorption values were not necessary, so that the washing could be dispensed with. The supernatant liquid was analyzed and the amount adsorbed was determined by difference. Experiments of this character were carried out with the potassium salts of oxalic, chromic and dichromic acids.

Adsorption of Oxalate Ion

Method of Analysis.—A solution of $N/50$ potassium oxalate was prepared in the usual way by direct weighing. This was used for standardizing a solution of potassium permanganate of similar concentration, which was subsequently employed to analyze for oxalate in the supernatant solution after precipitation. This standardization was effected in a volume of 150 cc in the presence of a constant amount of sulphuric acid and at a temperature of 70°. The analysis showed that 0.935 cc of permanganate was equivalent to 1 cc of oxalate.

Determination of Adsorption.—It was found that 8.25 cc of $N/50$ $K_2C_2O_4$ was necessary to precipitate completely 125 cc of colloid. The adsorption was determined at this concentration and at higher concentrations as shown in Table I. The final titrations were made with a 2 cc burette prepared from an Ostwald pipette. In the curve shown in Fig. 1 the amount adsorbed (in milliequivalents per gram of Fe_2O_3) is plotted against the concentration of electrolyte (in milliequivalents per liter) from which the precipitate separates.

The determination of adsorption with 15 cc of oxalate was repeated in the usual way except that the precipitate was washed once by shaking with 50 cc of distilled water followed by centrifuging for 10 minutes. The amount adsorbed was 12.24 cc as compared with 12.3 cc without the washing. This shows not only that the oxalate ion is strongly adsorbed but that little solution remains in the space occupied by the oxide after prolonged centrifuging.

TABLE I
Adsorption of Oxalate Ion

$KMnO_4$ to oxidize unadsorbed $K_2C_2O_4$ cc			$N/50$ potassium oxalate cc			Concentra- of electro- lyte (milli- equivalents per liter)	Amount ad- sorbed (milli- equivalents per gram Fe_2O_3)
I	II	Av.	Taken	Re- maining	Ad- sorbed		
0.27	0.25	0.260	8.25	0.28	7.97	1.238*	0.7000
0.26	0.26	0.260	8.75	0.28	8.47	1.308	0.7430
0.30	0.27	0.285	9.25	0.30	8.95	1.378	0.7807
0.35	0.30	0.325	9.75	0.34	9.41	1.447	0.8254
0.45	0.47	0.465	10.75	0.50	10.25	1.584	0.9000
0.84	0.87	0.855	12.00	0.84	11.08	1.752	0.9720
1.70	1.68	1.690	13.50	1.80	11.70	1.949	1.0263
2.50	2.54	2.520	15.00	2.70	12.30	2.144	1.0790

* Precipitation concentration

Adsorption of Chromate Ion

Method of Analysis.—A solution of sodium chromate $N/50$ with respect to chromate ion was prepared using the volumetric method of Seubert and Hinke[1] to make the analyses. The method of procedure was identical with that described in detail in earlier investigations.[2] It consists essentially in liberating iodine from potassium iodide by the action of chromate in acid solution—the liberated iodine being titrated with standard thiosulphate. A fiftieth molar solution of thiosulphate solution was employed. The standard solutions bore the following relationship to each other: 2 cc K_2CrO_4 = 3 cc $Na_2S_2O_3$.

Adsorption of Chromate Ion.—It was found that 9.50 cc of the chromate solution would just precipitate 125 cc of the colloidal oxide. Adsorption experiments were carried out at this and greater concentrations. A 10 cc burette was used in making the final titrations. The results are given in Table II and plotted in Fig. 1.

[1] Zeit. anorg. Chem., **14,** 1147 (1902).
[2] Weiser and Middleton: Jour Phys. Chem., **24,** 57, 645 (1920).

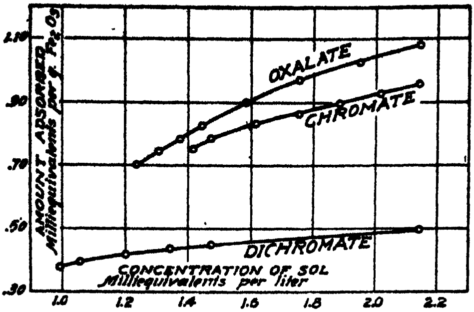

Fig. 1

The adsorption in the presence of 15 cc of chromate was determined, washing the precipitate before making the final

TABLE II

Adsorption of Chromate Ion

$N/50$ $Na_2S_2O_3$ required cc	$N/50$ potassium chromate cc			Concentration of electrolyte (milliequivalents per liter)	Amount adsorbed (milliequivalents per gram Fe_2O_3)
	Taken	Remaining	Adsorbed		
1.43	9.50	0.95	8.55	1.413*	0.7500
1.53	10.00	1.03	8.97	1.474	0.7869
2.28	11.00	1.52	9.48	1.618	0.8316
3.20	12.00	2.13	9.87	1.752	0.8658
4.16	13.00	2.77	10.23	1.885	0.8974
5.12	14.00	3.41	10.59	2.015	0.9290
6.15	15.00	4.10	10.90	2.144	0.9570

* Precipitation value.

analysis. The adsorption was slightly less, 10.70 cc as compared with 10.90 cc, the value obtained without washing.

Adsorption of Dichromate Ion

Method of Analysis.—A solution of sodium dichromate $N/50$ with respect to dichromate ion was prepared using the same method of analysis as with chromate. In this case 1 cc $K_2Cr_2O_7$ is equivalent to 3 cc of $Na_2S_2O_3$.

Determination of Adsorption.—6.50 cc of $N/50$ dichromate was required to precipitate 125 cc of colloid. The adsorption

at this and higher concentrations was determined in the usual way. The results are given in Table III and plotted in Fig. 1.

TABLE III
Adsorption of Dichromate Ion

$N/50$ $Na_2S_2O_3$ required cc	$N/50$ potassium dichromate cc			Concentration of electrolyte (milliequivalents per liter)	Amount adsorbed (milliequivalents per gram Fe_2O_3)
	Taken	Remaining	Adsorbed		
3.18	6.50	1.06	5.44	0.990*	0.3778
4.00	7.00	1.33	5.67	1.061	0.3938
6.10	8.00	2.03	5.97	1.203	0.4146
8.38	9.00	2.79	6.21	1.343	0.4313
10.80	10.00	3.60	6.40	1.474	0.4444
23.70	15.00	7.90	7.10	2.144	0.4930

* Precipitation value.

The adsorption was determined in the presence of 15 cc of electrolyte, washing the precipitate before the final analysis. 6.10 cc was adsorbed as compared with 7.10 when the precipitate was not washed. The ion was adsorbed less strongly than oxalate and chromate and more was removed from the precipitate by washing.

Discussion of Results

The results of the experiments above described emphasize the importance of adsorption by the neutralized particles in determining the amount of electrolyte carried down by a precipitated colloid. Take the case of oxalate ion: The addition of 8.25 cc of $N/50$ potassium oxalate was just sufficient to cause coagulation of 125 cc of colloidal ferric oxide within an hour. Of this amount of electrolyte, but 0.3 cc was not adsorbed. When 8.75, 9.25 and 9.75 cc, respectively, were added to the colloid, the same amount, 0.3 cc, remained unadsorbed. On gradually increasing the concentration of electrolyte, the amount unadsorbed increased; but this was less than 1 cc even when 12 cc of electrolyte were added. In the presence of 15 cc, 1.5 times as much electrolyte was carried down as at the precipitation concentration and the adsorp-

tion was so strong that but a trace of the 12.5 cc was removed by washing. Moreover, the adsorption had not reached the saturation value as is evident from the adsorption isotherm, Fig 1. The experiments with chromate and dichromate ions gave similar results. The increasing amount of electrolyte adsorbed above the precipitation concentration was all due to adsorption by the electrically neutral particles; and it is altogether likely that a large part of the electrolyte carried down at the precipitation value was adsorbed during agglomeration. It is obviously incorrect to assume as Freundlich does that equivalent amounts are adsorbed at the precipitation concentration, since this would mean either that the neutralized particles do not act as an adsorbent or adsorb all ions to the same extent. On account of adsorption during agglomeration it has been deduced[1] that equivalent amounts of various ions should not be carried down at the precipitation concentration on account of the variability of the latter and the consequent variability in the degree of saturation of the adsorbent by the adsorbed phase. The experimental results above described confirm this conclusion. Instead of having equivalent amounts adsorbed at the precipitation value of oxalate, dichromate and chromate ions, the adsorption is in the ratio 7.97 : 5.44 : 8.55.

Further consideration of the results disclose that the ion which has the highest precipitation value is adsorbed most at this concentration whereas one should expect the ion which precipitates in highest concentration to be adsorbed least. This behavior is readily understood when we consider that the adsorption of neutral particles during agglomeration was so great that but little of the electrolytes remained unadsorbed at their precipitation value. Obviously, under these conditions the elctrolyte with the greatest precipitation value will be adsorbed the most at this concentration—again emphasizing the impossibility of obtaining comparable adsorption values in the immediate region of the precipitation value.[2]

[1] Weiser and Middleton: Loc. cit.

[2] Weiser and Middleton: Jour. Phys Chem., **24,** 43 (1920).

Since the adsorption by neutralized colloidal particles during agglomeration is not negligible in any case and may rise to large proportions, we have the experimental evidence for the theory outlined to account for the so-called "acclimatization" phenomenon. From this point of view the term is a misnomer since the colloid does not become acclimatized to the presence of electrolyte in the ordinary sense. The necessity for using more electrolyte to effect complete precipitation on slow addition arises not from the adaptability of the colloid to the presence of electrolyte but from the fact that the fractional precipitation during slow addition continually removes ions owing to adsorption by neutralized particles; and this loss must be compensated for. The factors which determine the excess required for a given slow rate of addition are (1) the extent to which the colloid undergoes fractional precipitation, (2) the adsorbing power of the precipitated colloid and, (3) the adsorbability of the precipitating ion.

Summary

The results of this investigation may be summarized briefly as follows:

(1) The amount of electrolyte required to coagulate a colloid is influenced by the rate of addition. Since a quantity of electrolyte that will cause complete coagulation when the addition is rapid will not cause complete coagulation when the addition is slow, the colloid is said to become acclimatized and the phenomenon is called "acclimatization." The term is a misnomer since the colloid does not become "acclimatized" to the presence of electrolyte in the ordinary sense.

(2) The amount of precipitating ion carried down by a colloid is determined by (*a*) the adsorption of the electrically charged particles during neutralization and (*b*) the adsorption of the electrically neutral particles during agglomeration.

(3) The adsorption of oxalate, chromate and dichromate ions by colloidal hydrous ferric oxide has been determined at the precipitation value and at several concentrations above the precipitation value of the respective ions. The results em-

phasize the importance of adsorption by neutralized particles in determining the amount of electrolyte carried down by a precipitated colloid.

(4) The dropwise addition of an electrolyte to a colloid throughout a prolonged period is accompanied by fractional precipitation of the colloid. For a given rate of addition, the extent of this fractional precipitation depends on the nature of the colloid and the precipitating ion.

(5) The precipitation value is such a concentration of precipitating ion added all at once that sufficient adsorption to cause neutralization of the colloidal particles can take place promptly. The necessity for using more electolyte to effect complete precipitation on slow addition arises not from the adaptability of the colloid to the presence of electrolyte but from the fact that the fractional precipitation during slow addition continually removes ions owing to adsorption by neutralized particles during agglomeration; and this loss must be compensated for.

(6) The factors which determine the excess electrolyte required for a given slow rate of addition are, (*a*) the extent to which the colloid undergoes fractional precipitation, (*b*) the adsorbing power of the precipitated colloid and, (*c*) the adsorbability of the precipitating ion.

(7) The amounts adsorbed at the precipitation concentration of the various ions are not equivalent as Freundlich assumes. Adsorption of equivalent amounts effect neutralization of the charged particles; but adsorption during agglomeration varies with the concentration and adsorbability of the ion. Comparable adsorption values cannot be obtained at the precipitation concentration on account of the variability of the latter.

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ON THE PREPARATION OF COLLOIDAL MANGANESE DIOXIDE

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Three methods have this far been employed for the preparation of colloidal manganese dioxide.

I. The reduction of potassium permanganate. Marck[1] used hydrogen peroxide as the reducing agent; Spring and de Boeck[2] sodium thiosulphate; and Deisz[3] arsenious acid. Frémy[4] obtained a red solution of manganese dioxide, by treating potassium permanganate with concentrated sulphuric acid. He could not determine, however, whether he was dealing with a true or a colloidal solution.

II. The oxidation of manganous salts. Van Bemmelen[5] used chlorine as the oxidizing agent. Trillat,[6] using protective colloids such as albumin, gelatine, gum arabic, dexterine, etc., claims to have prepared colloidal manganese dioxide merely by exposing to the air alkaline solutions of manganous salts. He adduces, however, no conclusive evidence to prove that he was not dealing with complex organic salts such as complex copper glycerate $C_3H_5(OH)_2.O.Cu.O.C_3H_5(OH)_2$, complex copper tartrate

$$
\begin{array}{ccccccc}
Na - COO.CH & - & CH - COO.Na \\
| & & | \\
O & - Cu - & O
\end{array}
$$

III. Advantage is taken of the fact that MnO_2 is a reversible colloid. By carefully washing freshly precipitated manganese dioxide with conductivity water, Gorgeu,[7] and also Spring and de Boeck[2] were able to obtain colloidal solutions.

Of course, of the three methods, the last is the most difficult, since colloidal manganese dioxide is readily coagulated by salts. In the colloidal solutions as prepared by the other two methods there are present besides the MnO_2 and the KOH formed during the reduction of the $KMnO_4$ (which, however, has no appreciable coagulating effect since colloidal MnO_2 is negatively changed) other substances, as for example, Na_2SO_3, As_2O_5, and in Trillat's experiments, other colloids.

It seemed to us, therefore, worth while to make a brief summary of a new method of preparing colloidal MnO_2, which we developed while carrying out another investigation.

Potassium permanganate is a powerful but relatively slow oxidizing agent. For example, it does not oxidize Sörensen's salt[8] ($Na_2C_2O_4$) at ordinary temperatures, while it oxidizes completely at about 70° C. Similarly, potassium permanganate does not react at a measurable rate with NH_4OH at ordinary temperatures. If, however, to a hot concentrated $KMnO_4$ solution NH_4OH is added, NH_3 is oxidized to nitrogen and MnO_2 precipitates. If to a fairly dilute solution of $KMnO_4$, concentrated NH_4OH is added slowly, MnO_2 does not precipitate but remains in the colloidal form. After trying various concentrations of $KMnO_4$ and of NH_4OH we obtained best results by the following method:

Heat a $M/100$ permanganate solution to boiling. Then, while stirring, add concentrated NH_4OH one drop every 3 or 4 minutes. At no time should anything but the faintest smell of ammonia be perceptible. The solution should be kept at about 90° C. The solution gradually turns wine-red and finally coffee-brown by transmitted light and of a bluish brown oily color by reflected light. To test if all the permanganate has been reduced, a little of the colloidal solution can be coagulated by the addition of salt to show the presence of any violet color which might have been masked by the MnO_2. The intermediate red color may perhaps be due to the red form of MnO_2 which Frémy observed.

This reaction may possibly be made available as a qualitative or quantitative means of determining ammonia and ammonium salts. As will be seen from the equation $2KMnO_4 + 2NH_3 \longrightarrow N_2 + 2MnO_2 + 2KOH$ or $2MnO_4^- + 2NH_4^+ \longrightarrow N_2 + 2MnO_2 + 4H_2O$ in the final colloid there is present beside the MnO_2 only some KOH which, however, has a very small, if any, coagulating effect.[1] This method eliminates the necessity of removing the electrolyte by dialysis, especially since, as Marck has found the colloid is coagulated by coming in contact with filter paper or parchment, so it cannot be dialyzed unless very special precautions are taken.

This colloid at all concentrations catalyses the decomposition of H_2O_2. The concentrated solutions are coagulated during the reaction while dilute solutions are unaffected.

We also found that varying amounts of this colloidal solution may be added to alcohol or alcohol added to the solution so that the ratio of H_2O to alcohol may vary all the way from zero to infinity without coagulating the colloid.

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NEW BOOKS

A Treatise on Chemistry. *By H. E. Roscoe and C. Schorlemmer. Fifth edition completely revised by J. C. Cain. Vol. I, 21 × 15 cm; pp. xv + 968. New York: Macmillan and Co., Ltd., 1920. Price: $6.00.*—It would be a very good thing if each one of us were to read over the standard books like Roscoe and Schorlemmer about every so often because, with changing points of view, we should find things which had escaped us the time before. Ordinarily we do not do this and consequently the appearance of a new edition is very welcome because it makes us do what we ought to do. The reviewer has been delighted at the number of things he found that were of special interest to him and which he had either never known or had forgotten.

On p. 47 copper and sulphur are recommended to show the difference between a mixture and a compound. "When powdered sulphur and fine copper-filings are well mixed together, a green-colored powder results, in which, however, a microscope will show the particles of sulphur lying by the side of the particles of copper." Why should the powder be greenish? Red and yellow should give orange. The only guess one can make is that the blue surface color of copper plays a part and that suggests all sorts of interesting possibilities.

Iodine vapor, p. 229, is a splendid deep blue color by transmitted light when it is chemically pure but becomes reddish violet when mixed with air (Stas). One would like to know why. "When an electric discharge is passed through a heated Geissler's vacuum-tube containing a trace of iodine vapor, a spectrum of bright lines is obtained, characteristic of this element. This emission spectrum, however, does not correspond with the characteristic absorption-spectrum of iodine, so carefully mapped by Thalén, and seen when white light is passed through iodine vapor. Salet has shown that when an electric current of feeble tension is passed through a Geissler's tube containing iodine, another set of bright bands is obtained which are identical in position with the dark bands of Thalén's absorption-spectrum, each bright band being replaced by a black band when the vapor is illuminated from behind."

The substances which lower the decomposition temperature of potassium chlorate to the greatest extent, p. 243, are all known to be capable of existing in a higher state of oxidation, and "it appears probable that in these cases an alternate formation and decomposition of the higher oxide and decomposition of the latter into oxygen and the original oxide takes place. McLeod has shown by means of the microscope that the particles of manganese dioxide are broken up and attacked during the reaction, and has further found that potassium permanganate is formed in small quantity. He, therefore, suggested that the primary reaction is as follows:

$$2\ KCO_3 + 2\ MnO_2 = 2\ KMnO_4 + Cl_2 + O_2,$$

the permanganate being then broken up by the combined action of heat and of the chlorine produced simultaneously with formation of potassium chloride and oxygen and regeneration of manganese dioxide. It has been shown, however, by Sodeau, that this cannot represent the chief reaction, although it probably takes place to a small extent, and may form the source of the chlorine evolved."

"Sorby has shown that, when contained in thin capillary glass tubes, water may be cooled to—15° without freezing, while Boussingault has exposed water contained in a closed steel cylinder to a temperature of—24° for several days in succession without its freezing," p. 303.

On p. 192 there is the interesting fact that dilute solutions of chlorine in water are decomposed by tropical sunlight, while solutions containing more than six percent of chlorine are not attacked perceptibly. On p. 350 it is pointed out that "aqueous hypochlorous acid dissolves iron and aluminum with production of hydrogen and chlorine, while chlorine and oxygen are evolved with copper, nickel and cobalt, and magnesium yields pure hydrogen." These matters should be studied in detail.

"The flame of burning sulphur exhibits a continuous spectrum; but if a small quantity of sulphur vapor be brought into a hydrogen flame, a series of bright bands is seen when the blue cone in the interior of the flame is examined or when the sulphurized flame impinges on any cold surface. This blue tint is almost always seen when a pure hydrogen flame is brought for an instant against a piece of porcelain, the blue color being produced, according to Barrett, by the sulphur contained in the dust in the air," p 387.

"Sulphur dioxide has been shown by Tyndall to undergo a remarkable decomposition when exposed to light. If a beam of sunlight be passed through a long tube filled with the colorless gas, a white cloud is seen to make its appearance and this consists of finely divided particles of sulphur and sulphur trioxide which are separated by the chemical action of the light," p. 405. Sulphur dissolves in liquid sulphur trioxide below 15° to form blue drops which later solidify to "bluish green crystalline crusts closely resembling malachite in color," p. 450. One wonders whether the formation of S_2O_3 in the upper atmosphere after volcanic outbursts can have anything to do with the phenomenon of the blue sun.

It does not seem possible that one cannot determine what compound gives the smell of rotten horse-radish when selenium burns, p. 472. The golden yellow color of tellurium vapor, p. 485, should be correlated with the color of tellurium hydrosols. One wonders how many of the alleged boron hydrides, p 726, really exist. Arsenic disulphide is said to have a resinous lustre, p. 708, and coal a fatty lustre, p. 768; but there is no definition of the seterms. Argo's method of making fluorine is given, p. 167; but the war-time manufacture of phosgene is not mentioned, p. 833, and the editor apparently does not know that phosphorus is made at Niagara Falls, p 621. One would like to know why melted phosphorus remains supercooled for an especially long time "when it is allowed to cool slowly under a layer of an alkaline liquid or when the solution in carbon bisulphide is evaporated slowly under water," p 622. It is interesting to learn that red phosphorus was precipitated from a hydrogen flame on a cold plate as long ago as 1856, p. 634. It was new to the reviewer that an acid solution of copper and iron salts and an acid solution of chromic acid are sold under the trade names "frankolene" and "heratol" when adsorbed in kieselguhr, p. 900.

"The spores of moulds are so light that the isolated cells can float freely in the atmosphere. The conditions are otherwise in regard to bacteria. These are not found isolated in the air, but aggregated in small groups and adhering to particles of dust. Dust is the vehicle by which they are transmitted to the

air, and the bacteria therefore belong to the more ponderable elements of the air-dust. Thus, for instance, if the dust in a room be stirred up, large numbers of bacteria will be found in the air; but after the dust has once again settled to the ground, the bacteria disappear in great part, leaving the lighter free spores of the moulds in the air.

"Bacteria do not pass into the air from a moist surface or from the surface of water. Indeed the air of sewers is found to contain fewer organisms than the outside air, the damp walls and the sewage retaining the organisms which are not carried about by wind. It is only when the surface containing them becomes dry that the wind is able to carry up dust and with it bacteria. The factors favouring the distribution of bacteria in the air are dryness of the soil and wind currents; the factors hindering their presence are moistness of the soil and a still atmosphere. The number of microbes present in the air will, accordingly, vary with the atmospheric conditions. The air contains few microbes after a prolonged fall of rain, and many after prolonged heat and dry weather. The spores of moulds, however, form an exception to this rule, as they are most abundant in the air during damp weather, moisture favouring their production. The less dust there is in the air, the less the number of bacteria, and *vice-versa*. The air over the open sea and on high mountains contains few or no bacteria; the air of a town more than the air of the country. Drying being essential to the passage of microbes into the air, the forms most largely present will be those least affected by dryness *e. g.*, moulds and their spores. In the open air from 10 to 20 times as many moulds are found as bacteria. On the other hand, drying is fatal to a large number of bacteria, and especially to the pathogenic organisms, *e. g.*, Koch's comma bacillus, glanders bacillus, etc. It would therefore seem that the dangers of air infection have been over-estimated. The air of enclosed spaces and dwelling houses is richer in microbes than the open air.

"It thus appears that the most dangerous factor, hygienically, is not the air itself or the gases and sewage emanations that may be present in it, but the dust to which bacteria cling. The dust of dwellings may, therefore, become an important factor in carrying infectious microbes, more especially by fragments of clothing, linen, etc., from sick people and their attendants. Cornet found that the dust of dwellings contains the tubercle bacillus, and that such dust can produce an infection with tubercle. The dust in the air of dwellings and hospitals is infectious for animals, and may produce tubercle, malignant oedema, tetanus, or septic peritonis," p. 614.

If others get as much out of this first volume as the reviewer has, the book will not lack for readers.

Wilder D. Bancroft

The Chemistry of Synthetic Drugs. *By Percy May. Third edition. 22 × 14 cm; pp. xv + 248. New York: Longmans, Green and Co., 1921. Price: $4 25.* —In the preface the author says: "On the whole the knowledge gained during the war seems to emphasize the incompleteness of the theories connecting chemical constitution and physiological action, and too much stress cannot be laid on the narrowness of their scope and on their tentative and provisional nature. Nevertheless, their usefulness should not be denied, and they justify their existence as long as they suggest new and fertile lines of research. None of them, however,

are sufficiently complete to enable the physiological effect of a new substance to be forecast beforehand with certainty, and in all cases it must be tested by experiment."

The physical chemist is interested in the general theories of the action of narcotic drugs, pp. 44–49; in the preparation of eukodal by reduction with hydrogen in the presence of palladium, p. 63; and also in the following paragraphs, pp. 94, 171.

"Cocaine has several disadvantages when used for hypodermic injection, one of the most serious being that its solutions do not keep well, but become mouldy and decompose on boiling, so that they cannot be readily sterilized. For this reason, and also on account of the high price of cocaine, various attempts have been made to prepare analogous compounds which it was hoped would resemble cocaine in its useful physiological effects. As cocaine is a derivative of ecgonine, which is closely related to tropine, and as atropine, one of the esters of tropine, has a slight anaesthetic action, various attempts have been made to prepare substances from tropine which should have an action resembling that of cocaine. Several synthetic tropeines have been prepared, and have already been discussed, but none of these are of value as substitutes for cocaine. Strangely enough, however, a natural tropeine was discovered in Java, coca leaves, which is a stronger local anaesthetic than cocaine. This substance, which is called tropacocaine, also has the advantage over cocaine in being less toxic and more resistant to micro-organisms, and hence its solutions can be preserved for some length of time. It is the benzoyl ester of pseudo-tropine which only differs from ordinary tropine in its space configuration. It differs from cocaine and atropine in having no mydriatic action, and in this respect it resembles the other pseudo-tropeines, such as those of mandelic acid and tropic acid. It will thus be seen that the tropeines derived from tropine itself have a strong mydriatic action, but only a weak anaesthetic action, while their stereoisomerides, derived from pseudo-tropine, have no mydriatic action, but are powerful local anesthetics.

"Our knowledge of the chemical specifics and their probable mode of action, we mainly owe to Ehrlich, and his success in this field was largely due to a careful study of the reactions between the parasites and the dyes which reveal them in their surroundings. He realized that the relation between a dye and a particular type of cell is a chemical fact of great importance, and that such a dye must contain an anchoring group that can enable it to attach itself to the particular type of cell in question. To vary the simile, the chemical specific may be likened to a poisoned arrow, the point being the particular dye which has a selective affinity for the parasite, and therefore fixes it. If a poison can be attached to such a dye or to the anchoring group of such a dye, the arrow will be not merely a dye, but also the desired chemical specific. This procedure is not so simple as might be gathered from the above, as the attachment of a poisonous element or radicle may destroy the anchoring effect of the other groups. On the other hand, many dyes are themselves poisonous to certain parasites, and act as chemical specifics in these particular infections."

Some of the colloidal solutions are interesting, pp. 193, 194. "Argonin is a compound of silver and casein, but is difficultly soluble in water and sensitive to light. Protargol is a compound of this type which has a higher percentage

of silver, is free from caustic effects, does not precipitate chlorides, and has the bactericidal effects of silver. To prepare it, a peptone solution is precipitated with silver nitrate solution or shaken with moist silver oxide and the insoluble compound thus obtained, digested with protalbumose. Soluble protargol is formed in this way, and is separated from the solution by evaporation *in vacuo*. Similar compounds can be obtained from plant globulins, and the corresponding compounds have also been obtained from mercury, iron, copper, lead, zinc, and bismuth. Other silver albumin compounds have been obtained from gelatoses (hydrolytic products from glue). Albargin, a powder readily soluble in water and of neutral reaction, is a substance of this type. It is recommended in various septic conditions as a non-irritant antiseptic."

"Ferric salts resemble those of aluminium in many of their properties, and they are used as astringents and styptics. For use as a styptic, a double compound of ferric chloride and antipyrine has been introduced under the name of Ferripyrin, but it has no advantages compared with ferric chloride itself.

"The chief therapeutic use of iron is, however, in anaemia and chlorosis. For this purpose, the ferrous salts are usually preferred, as they do not have so great a caustic action as the ferric, and hence do not disturb the stomach so much. The unpleasant by-effects of iron on the teeth and stomach have led to many attempts at obtaining compounds which should be free from these disadvantages.

"By the reduction of haemoglobin, Kobert obtained a substance, haemol, which contains the iron in the same form as haemoglobin, and Bunge obtained from egg-yolk a substance from which the iron could not be precipitated by ammonium sulphide. This substance was termed haematogen by Bunge, and a similar substance has been isolated from the liver. A synthetic albuminate of iron was obtained by Schmiedeberg, but this differs from Bunge's haematogen in certain respects. Various other albuminates of iron have been prepared, and many of these, as well as some of the foregoing substances, have been placed upon the market (Haemol, Haematogen, etc.). None of these organic compounds are any more powerful agents in the treatment of anaemia than the simple inorganic salts, their advantage being simply that they are less irritant to the gastro-intestinal tract."

The following conclusions, p. 214, are worth quoting. "None of the compounds which have been tried up to the present fulfil all the conditions necessary for a really efficient trypanocide. These conditions may be summed up as follows:

"(1) The compounds must be non-irritant, and capable of remaining in perfect solution at the temperature and alkalinity of the tissues.

"(2) It must act quickly on the trypanosomes before they can acquire a tolerance to the drug.

"(3) When the trypanosomes have been expelled from the blood by a single full therapeutic dose, there must be no recurrence in the majority of cases within some fixed time, which will depend to some extent on the particular host experimented with, and on the strain of parasites used.

"Although the arsenic compounds which have been described do not fulfil the second and third of these conditions, yet the majority of them fulfil the first of these quite admirably but in the case of antimony difficulty has been experienced in obtaining derivatives to fulfil even this condition.

"Of the various compounds which have been tried therapeutically, those of a similar nature to ordinary tartar emetic (potassium antimonyl tartrate) are among those giving the best results. Thomson and Cushny have experimented with many compounds of this type derived from various hydroxyl acids, and the best results were obtained with compounds prepared from tartaric and malic acids. The sodium and potassium antimonyl-tartarates seemed to be very nearly equal in their efficiency, but the ethyl ester of antimonyl-tartaric acid appeared to have some advantage over these alkali salts. Potassium ammonium antimonyl-tartrate is known as Antiluetin." *Wilder D. Bancroft*

Vitamines. *By Benjamin Harrow: 18 × 13 cm; pp. x + 219. New York: E. P. Dutton and Co., 1921. Price: $2.50.*—Three vitamines are recognized at present: fat-soluble A, water-soluble B, and water-soluble C, p. 166. Fat-soluble A is present in abundance in milk, butter, and egg-yolk; to a lesser extent in beef fat and in many vegetable foods such as lettuce, spinach, cabbage, carrots, potatoes, etc. Lard and vegetable oils, such as olive oil, are devoid of it. Cereals in general (wheat, rye, barley, etc.) contain little. In a general way the statement mav be made that this vitamine is present in green leaves in the embryos of many seeds. Water-soluble B is more abundant than either of the other two. In fact, nearly all natural foods contain some of it.

Yeast is particularly rich in this vitamine and so are milk and orange juice.

The cereals contain it but only in the outer layers so that vitamine B is absent in patent flour though present in whole wheat flour. Most fresh fruit and fresh vegetables contain water-soluble C.

"All three vitamines are more or less susceptible to heat, so that any process involving this operation—cooking or canning—is apt to destroy, or lessen greatly the efficacy of the vitamine. Of the three, water-soluble C seems the most susceptible and water-soluble B the least. One of the problems of the immediate future is to devise methods of drying, preserving, and canning food, without at the same time lessening the vitamine value of such foods," p. 167.

Professor Bottomley has noticed that whenever peat is attacked by soil bacteria so that it decays, plant vitamines appear in much force. "Such a decomposing peat can be shaken with water, and the watery extract can then be shown to stimulate plant growth and also to stimulate soil bacteria, particularly the types that bring about the decomposition of peat. This has led to the suggestion that the plant vitamines—and in the ultimate analysis this would include the animal vitamines—are actually produced by soil-organisms.

"To suppcrt his contention, Professor Bottomley has performed an experiment which illustrates how, whenever the bacterial activity in the soil increases, we get a corresponding increase in vitamine activity. The organic manures usually applied in agriculture, such as leaf mold and stable manure, were examined. They all contained varying proportions of water-soluble vitamine corresponding to the water-soluble B variety with which we are already familiar. But in every instance an extract of well-rotted manure, where bacteria are particularly abundant, was far more effective in bringing about growth in plants than an extract of fresh manure. Just as with the vitamines the animal needs, the amount of plant vitamine that the plant needs is so small that such an addition to the plant nutrition cannot materially add to their calorific value," p. 114.

"Dr. Seidell, of the U. S. Department of Hygiene, and Dr. Harden, of the Lister Institute, London, have shown how by the use of fuller's earth, a common laboratory chemical, and other substances closely related to it, the antineuritic vitamine in orange juice can be removed completely, leaving only the antiscorbutic. Note how such an experiment can be carried out. Your orange juice in sufficient quantities cures scurvy and cures beriberi, which means that the orange contains both vitamines responsible for such cures. You now mix your orange juice with fuller's earth and shake. You next withdraw the fuller's earth and you find that it has acquired the property of curing beriberi, but not scurvy. Before mixing the orange juice with fuller's earth the latter cured neither the one nor the other disease. Fuller's earth, by being mixed with orange juice, must have absorbed the antineuritic vitamine. The solution that is left after the fuller's earth has been removed has the power of curing scurvy, but not beriberi. Hence we conclude that the antiscorbutic vitamine has not been removed by the chemical," p. 147.

"How specific in behavior these vitamines are may be illustrated in an account taken from the siege of Kut. For four months, from December, 1915, to April, 1916, British and Indian troops were besieged by the Turks. During this period the food of the British consisted of white flour or biscuits, tinned meats and horse flesh. The Indians refused to eat fresh meat (horse flesh), but ate *ata* or barley flour instead. The Indians developed scurvy and the British beriberi. Why? The nature of the cereal diet (rich in water-soluble B) protected the Indian troops from beriberi, but not from scurvy. On the other hand, the fresh meat the British troops ate protected them from scurvy, for the meat contained water-soluble C, but there was nothing in their diet to supply the water-soluble B. The white flour and biscuits are practically free from water-soluble B.

"In the northern parts of Russia scurvy makes its appearance quite regularly every year; yet the Allied troops sent to support the Anti-Bolsheviks were quite free from it. This is due to the fact that the British Government allowed itself to be guided, in its choice of food for soldiers, by the British leaders in nutrition. Professors Bayliss and Starling and Hopkins and Harden and Miss Chick have all been able exponents of the vitamine hypothesis. On their advice the Allied soldiers in Russia were allowed liberal amounts of such foods as soured milk, fresh meat, fresh lemon juice, etc. The results amply confirmed the claim made that scurvy is a deficiency disease due to the absence of one of the necessary vitamines," p. 148.

"We must be careful in advocating certain diets to remember that man is not altogether a machine. The results of experiments in physiology and chemistry cannot always be applied in their entirety. You may discover from such experiments that milk is the most important of foods; yet the fact remains that there are people who dislike it, and who, therefore, because of such dislike, do not derive as much benefit from drinking milk as others who have no such dislike. I know (and you know) persons who dislike butter; others who dislike vegetables prepared in a certain way—they may like fried, but not mashed potatoes. Some like pot roast and others hate the sight of it. Some relish cheese full of odors, and others are ready to vomit at the mere mention of the name. And then you have variations in taste due to differences of re-

ligion, of race, of country. Watch the orthodox Jew make faces when he sees ham or pork. Watch the uninitiated American observe caution when he first attacks chop suey. Watch the Englishman throw up his hands in holy horror when his Spanish friends swallow garlic and onions," p. 182.

On p. 174 the author seems to imply that the difference between human milk and cow's milk may be a question of vitamines; but the work of Alexander makes it more probable that the important thing is the form in which the caseine coagulates. One is tempted to wonder whether very thin people do not have anti-vitamines somewhere inside them. It is possible that the problem of the fat man may be solved by serving suitably de-vitaminized food.

Wilder D. Bancroft

Chemical Reactions: Their Theory and Mechanism. *By K. George Falk. 20 × 14 cm; pp. ix + 211. New York: D. Van Nostrand Co., 1920. Price: $2.50.*—In the preface the author says: "The central idea of this book is the development of a general theory of reactions which will include both inorganic and organic reactions. The fundamental view upon which this theory is based is the 'addition' theory, according to which, when two or more substances react, a primary addition is the first step." This sort of thing is very desirable in principle. We are anxious to have monographs bringing our knowledge up to date and presenting it from a single point of view. The table of contents is almost alluring with its references to valence, coördination number, acids and bases, catalysis, olefines and their reaction products, oxidation and reduction, general considerations in regard to chemical reactions.

The book itself is rather disappointing, however, because it is so vague. We are told, p. 33, that calcium chloride may occur with two, four, or six of water of crystallization, which we knew before, and that the coördination number of the calcium in the hexahydrate is six. Calcium chloride combines with eight molecules of ammonia and the coördination number of calcium is eight in this compound. Why should it not be eight with water and what can one predict about calcium sulphate? The following statement on the same page is not very helpful: "The external physical conditions such as concentration, vapor pressure, and temperature, determine the number of molecules of water of hydration of calcium chloride. This shows that the coördination number of the calcium is dependent upon external conditions just as the ordinary valence is."

Under catalysis the author discusses some of the stock cases where intermediate compounds are formed; but he does not take up any of the interesting ones. On pp. 157 and 197 we are told that formic acid is hydrated carbon monoxide and therefore naturally splits off water with such catalysts as hydrochloric acid. With rhodium "the carbon atom of the formic acid is oxidized, two units of valence to form carbon dioxide, and one of the hydrogen atoms reduced two units of valence to form the neutral hydrogen molecule." Nothing could be simpler than that; but are we any wiser than we were before?

The author does not always play quite fair. On p. 66 he discusses Menschutkin's experiments on the effect of the solvent on the rate of reaction between triethyl amine and ethyl iodide. He concludes that the velocity is connected roughly with the unsaturation as ordinarily considered and that this relation is very nearly true if certain solvents are omitted. He makes no reference

to the fact that the order of the solvents is quite different with other reactions. The casual reader will get an utterly false idea of the situation from these pages.

A dozen pages or more are given to the Friedel and Crafts reaction; but there is nothing very definite to be got out of them. On p. 30 platinum is taken as the central atom in the ammoniates of platinic chloride; but, on p. 34, we are told that the nitrogen of the ammonia (except with the first two molecules of ammonia) may also be taken to be the central atom. It seems to the reviewer that Dr. Falk has never realized that it is not enough to show that things can be rewritten in terms of a new theory. It must either be shown that the new theory is the only one which accounts for the facts satisfactorily or that the new theory is an effective working hypothesis, enabling people to discover new facts or relations more readily. Dr. Falk has not made any attempt to do either of these things and consequently his book will not be very helpful.

Wilder D. Bancroft

Dictionary of Explosives. *By Arthur Marshall. 21 × 14 cm; pp. 14 + 159. Philadelphia: P. Blakiston's Son and Co., 1920. Price: $3.75.*—In the introduction the author says: "It is a generation since a dictionary of explosives has been published, and, in the meantime, many new explosives have been introduced. It is hoped, therefore, that this small volume, giving concise information about these special materials, may prove useful to those who have to deal with them. In Cundill and Thomson's 'Dictionary of Explosives,' issued in 1895, there are many entries of the names of inventors and of mixtures which had been proposed but have never been used commercially, nor are likely to be. As modern explosives were then in their infancy, it was no doubt wise to insert all the available information whether it appeared to be important or not; but now it seems to me better to restrict the scope of the dictionary so as to keep its size within moderate limits. Practically only explosives with special or proprietary names are therefore dealt with here. For information concerning chemical substances, such as the nitro-toluenes and other nitro-compounds, reference should be made to the text-books on explosives and chemistry.

"Explosives may be classified in various ways, according to the purpose of the classification, but the great majority of them fall naturally into two main divisions: propellants and high explosives. Propellants explode comparatively slowly, and are used to propel projectiles from fire-arms High explosives are much more rapid in their action, and are used for bursting and shattering. Propellants are of two sorts, according as they are intended for use in shot-guns or rifled fire-arms. Those for shot-guns burn more rapidly than those for the latter, but both practically always contain a considerable proportion of nitrocellulose, gelatinized by means of such solvents as acetone or ether-alcohol, according as it is of high or low nitration. Some contain also nitroglycerine, and are then called nitroglycerine powders, whereas those that do not contain this subtance are termed nitrocellulose powders. Many powders also contain other ingredients, as may be seen from the compositions given in this dictionary.

"Of high explosives an important class is used for charging shells and bombs As a rule, but not necessarily, these are not the same as the explosives used for mining operations and other general blasting purposes. Another important class is that of the coal-mine explosives, which are designed to give only a short

and comparatively cool flame so as to diminish the danger of igniting fire-damp and coal-dust. Nearly half the explosives in this dictionary are coal-mine explosives. The reason for this large number is that no finality has yet been reached as to the best and safest explosives to use in coal mines. When more experience has been gained it is probable that the number of these explosives on the market will be reduced. In England the Permitted List has already been cut down considerably.

"Another class of explosives that has not yet been mentioned is that of the primary igniters, of which fulminate of mercury may be taken as typical. The characteristic of these is that they can be exploded or ignited by a spark or moderate friction, and consequently they can be employed to fire other, less sensitive explosives. There are, however, practically no explosives of this class which possess special or proprietary names, and consequently they are not dealt with in the dictionary."

The reviewer is not qualified to say how good this dictionary is; but he has enjoyed glancing over the pages and he feels certain that a book covering this general ground is useful for reference.

Wilder D. Bancroft

American Lubricants. *By L. B. Lockhart. Second edition. 23 × 15 cm; pp. xi + 341. Easton: The Chemical Publishing Co., 1920. Price: $4.00.*—The first edition was reviewed over two years ago (**22,** 454). The new edition is about forty percent larger than the old one. There is a reference to the germ process of lubrication, p. 26 and to Holde's work on the physical condition of machine greases, p. 150. The reviewer would have welcomed a few words on the differences between soda and lime greases. There are new specifications for linseed oil, castor oil, steam cylinder oils, turbine oils, gas engine oils, transmission and cylinder oils, compressor oils, engine oils, printing and light machine oils, floor oils, boiler compounds and cotton waste, fuel oils, kerosene, gasolene, etc. The new edition is therefore indispensable to anybody who has found the first edition helpful. *Wilder D. Bancroft*

The Electric Furnace. *By Henri Moissan. Translated by Victor Lenher. Second edition. 23 × 15 cm; pp. xvi + 313. Easton: The Chemical Publishing Co., 1920. Price: $3.50.*—The first edition was published in 1904 (**9,** 156) and has been out of print. The second edition appears to be practically a reissue of the first, except that the bibliography of Moissan's papers has been extended. The extra material included in de Mouilpied's 1904 edition has not been put in and there is no index. It is a good thing to have this text once more available to students.

Wilder D. Bancroft

An Introduction to the Principles of Physical Chemistry. *By E. W. Washburn. Second edition. 21 × 15 cm; pp. xxvi + 518. New York: McGraw-Hill Book Co., 1921. Price: $3 50.*—In the preface of this edition the author says: "In preparing the second edition the author has adhered to the general plan and arrangement of subject matter adopted in the first edition. While some changes and additions have been made to practically every chapter in the book, the revision has consisted chiefly in the incorporation of new material

representing the scientific advances which have been made during the past six years."

On p. 17 under atomic weights the author divides the elements into two groups, those which are probably elements and those which are probably, or certainly, isotopic mixtures. The first group is rather small, consisting of aluminum, argon, beryllium (which the author calls glucinum), calcium, carbon, chromium, cobalt, fluorine, helium, iron, lithium, manganese, nitrogen, phosphorus, potassium, sodium, sulphur, and titanium. This list does not agree with that on p. 20, where hydrogen, oxygen and arsenic are given as pure elements while argon is put down as probably having two isotopes.

Bingham's work on plastic and viscous flow is new, p. 63; there are new values for some of the critical data, p. 73; Hildebrand's figures for internal pressures are included, p. 76. All the work on the internal structure of crystals, pp. 80–90, is new, and so is the discussion of the kineties of sublimation and condensation at crystal surfaces, pp. 94–97. The paragraphs on the quantum theory and on the third law of thermodynamics are new, pp. 141–143; but unfortunately we still find the unqualified statement, p. 139, that if any two phases are both in equilibrium with a third phase, they are in equilibrium with each other. Langmuir's view is adopted, p. 175, that oleic acid sticks out of water like worms out of wet earth.

The lime-alumina-silica diagram, p. 417, was not in the first edition. Most of the chapter on dispersed systems is new, pp. 422–448; the same is true of the chapter on atomic structure and the periodic system, pp. 456–474; and some of the chapter on radioactivity is new, pp. 449–455.

These references do not claim to cover all the changes; but they are sufficient to give an idea of the extent to which this edition has been revised. In some respects this volume is more human than its predecessor; but the general criticisms made previously by the reviewer (**20**, 454) still hold.

Wilder D. Bancroft

The Calculations of Analytical Chemistry. *By Edmund H. Miller. Third edition. 22 × 15 cm; pp. 201 + x. New York: The Macmillan Co., 1921. Price: $2.00.* The author's object is to furnish a text-book which gives the necessary information which every student of analytical chemistry should understand thoroughly before taking up advanced work. The chapters are entitled: calculation of chemical equivalents and atomic weights; calculation of formulae and percentage; calculations of mixtures having a common constituent; calculations from equations; calculation and use of factors; calculations of volumetric analysis; calculations of density of solids and liquids; calculations of gases; calculations of calorific power; electric and electrolytic calculations for direct currents. There are also twenty-five pages of tables. The title-page is dated 1921 and the preface 1904.

Wilder D. Bancroft

THE STATES OF IRON IN NITRIC ACID

BY JOSEPH GRANT BROWN

Two distinct states of metals with reference to their rate of dissolution have long been recognized. They have been termed the active and the passive. Iron, cobalt, tin, chromium, nickel, lead and other metals show these states definitely. Under some conditions a third state, called the semi-passive, is shown, although this state is not as definite as the others.

While a great amount of work has been done upon the subject, there is no general agreement as to what distinguishes the different states nor as to the process by which the change from one state to another takes place. Although it is probable that the cause of these states is the same in all cases, it is well known that there are a number of different conditions under which the change from one to another takes place. It would seem, therefore, that a solution of the problem can be expected only by making a detailed study of some one process.

Undoubtedly the dissolution of iron in nitric acid is one of the most complicated processes that could be selected; yet it has the advantage of a spontaneous change from one state to the other under ordinary conditions, and hence it has been chosen as the subject for such a study.

Historical

Numerous brief accounts of the action of nitric acid upon iron were published prior to 1865, but at that time Ordway[1] published a paper on "Nitrates of Iron" which gives the results of a great number of careful experiments. Work upon the action of metals on nitric acid has been done by Russell,[2] Divers,[3] Veley,[4] Armstrong and Ackworth[5] and others, but the most exhaustive study has been made by Freer and Higley.[6] Their work extended over several years and is reported in a series of papers entitled "The Action of Metals on Nitric Acid." The action of iron is given in their last paper[7] together with a summary of their work

on other metals, and some work on the electrolysis of nitric acid. The electrical conductivity of nitric acid has been measured for all concentrations by Veley and Manley.[8]

Papers dealing with the passive state of iron have been so numerous that several bibliographies have been compiled. Of these the most comprehensive is that of Heathcote.[9] A great deal of the work referred to in these bibliographies deals with the action of iron on nitric acid, but the material is scattered through a great many papers and hence it is not easy to determine just what has been done.

A paper by Young and Hogg[10] on "The Passivification of Iron by Nitric Acid" gives complete results upon the reaction velocity in acid of different density and definitely connects the passive state with certain products.

Chemical Action

A review of the chemical action of iron in nitric acid will be desirable before proceeding with a consideration of the states of iron. This will be limited to the action of pure iron in an excess of acid at room temperature, since these are the conditions under which the experimental work reported in this paper has been done.

Scheurer-Kestner[11] says that in 1.034 density acid only ferrous nitrate is formed; in 1.073 density acid both ferrous and ferric nitrate are formed; while in 1.115 density acid only ferric nitrate is formed.

Ordway found that in dilute acid, up to 1.05 density, the products of the reaction were ferrous nitrate, ammonium nitrate and a small amount of nitric oxide. In stronger acid, up to 1.20 density, he found principally ferric nitrate, small amounts of ferrous and ammonium nitrates, and a considerable amount of nitric oxide.

Freer and Higley paid no attention to the iron salts formed but made careful determinations of all the reduction products. The results of their experiments are shown in the accompanying curves (Fig. 1), in which the abscissas represent acid density and the ordinates represent the percent of equivalent

iron corresponding to the relative amount of the product formed in each case.

It must be remembered that these percents do not give the actual amounts of the products formed but only the relative amounts of each to the total products. In dilute acid the principal product is the ammonia and as the strength of the acid increases this product falls off and is not formed in acid of greater density than 1.26. Nitric oxide is also an important product of the reaction in dilute acid and it increases with the density up to about 1.28 when it begins to fall off and is not found in 1.40 acid. Small amounts of nitrogen and of nitrous oxide are formed, and these, like the nitric oxide, reach maxima

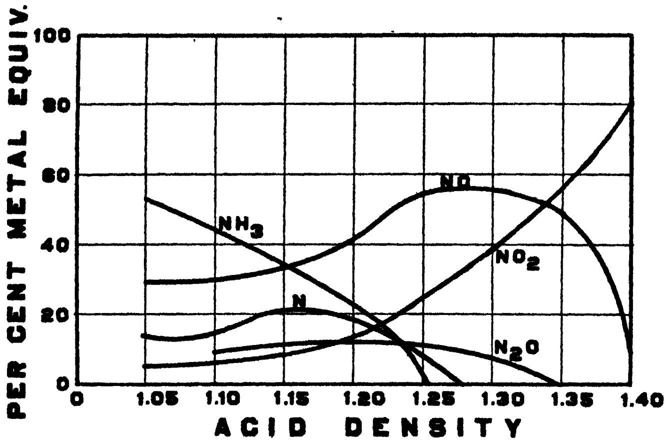

Fig 1

and disappear as the acid becomes denser. Only a small amount of nitrogen peroxide is formed in dilute acid, but this constantly increases with the density and in concentrated acid it is the only reduction product.

The mode of action of metals was carefully considered by Freer and Higley in connection with their work. They pointed out that there are two characteristic reactions, both of which result in the formation of reduction products. The first of

these, termed the nascent hydrogen reaction, is illustrated by the action of zinc upon dilute acid and it results in the greatest possible reduction of the acid:

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

The second reaction, termed direct deoxidation, is illustrated by the action of copper upon concentrated acid, and it results in the least possible reduction of the acid:

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

The fact that both ammonium nitrate and nitrogen peroxide are obtained when iron acts upon nitric acid shows that both of these reactions are present, the nascent hydrogen reaction being specially characteristic of dilute acid and the deoxidation reaction specially characteristic of concentrated acid. Freer and Higley think that the nitric oxide is a result of the action between nitrogen peroxide and water and that the nitrogen and nitrous oxide can be accounted for by a more complete reduction of the nitrogen peroxide by the iron.

The products obtained by the electrolysis of nitric acid with platinum electrodes are similar in many respects to those obtained by the action of iron (Fig. 2).

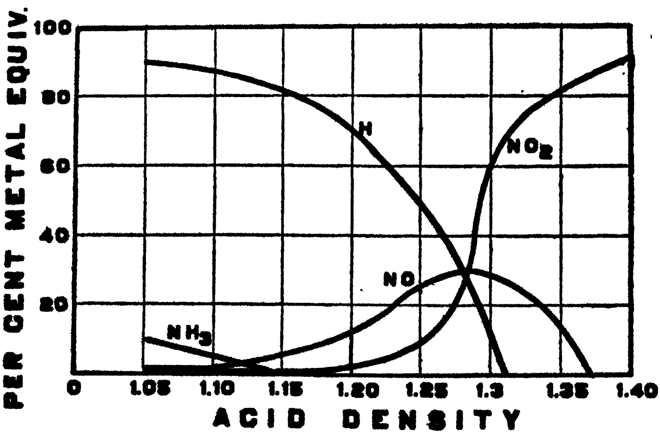

Fig. 2

Hydrogen is given off freely at the cathode in dilute acid but ceases to come off in acid slightly above 1.25 density. It begins to come off in acid of 1.30 density but suddenly ceases after a short time. Ammonia is the principal reduction product in dilute acid but ceases in 1.15 acid. It is noticeable that nitric oxide reaches a maximum and nitrogen peroxide increases rapidly in acid of 1.28 density; and that nitric oxide falls off and nitrogen peroxide becomes the only product in concentrated acid.

The reaction velocity experiments of Young and Hogg show a sudden change in the reaction velocity constant between densities of 1.25 and 1.26. Since this is the concentration which first produces the passive state, they termed it the "passive break." It is extremely significant that this density

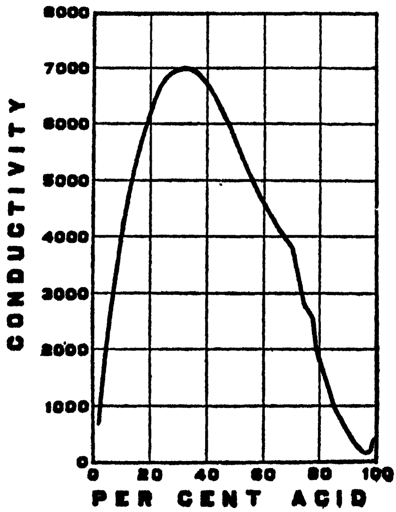

Fig. 3

corresponds closely with the density at which ammonium nitrate ceases to occur as a reduction product and hydrogen ceases to come off in electrolysis. Young and Hogg reached

the conclusion that nitrogen peroxide is the cause of the passive state but they did not feel that they could say why it should produce this state or what is the ultimate mechanism of the process.

The electrical conductivity of nitric acid at 15 degrees Centigrade was determined for all concentrations by Veley and Manley. Their curve is reproduced in Fig. 3.

The conductivity reaches a maximum in 30% acid, corresponding to a density of about 1.15, then falls off gradually to 70%, corresponding to a density of about 1.35, where it falls suddenly and becomes almost zero in 97% acid.

Experimental

It appears from the above that the action of iron on nitric acid has been studied rather fully from the standpoint of products and rate of reaction. In order to connect these results with the states of iron, it seemed desirable to make a more extensive study of the electro-chemical relations involved. Hence experimental work along this line has been undertaken and the results are given below.

In order to simplify matters as much as possible, the present work has been done with a voltaic cell. The advantages of such a cell are: that its electromotive force is a direct indicator of the state of the iron; the condition of the surrounding electrolyte may be readily observed; and practically no current needs to flow, so that polarizations due to electrolysis are eliminated.

The experiment consisted in forming the cell: Fe|HNO_3 solution | concentrated HNO_3 |Pt, and measuring its electromotive force from the instant the cell was formed until the electromotive force reached a steady value, both with the iron in motion and with the iron at rest. Observations were made with a low power microscope upon the changes which took place about the iron when it was brought to rest. This was done for the following series:

TABLE I

Acid density	Grams per cc.
1.01	.0109
1.09	.155
1.12	.202
1.17	.279
1.25	.398
1.32	.507
1.37	.594
1.41	.675

A great deal of preliminary work was necessary to find the conditions under which reliable results could be obtained. This included methods of treating the iron, the form and makeup of the voltaic cell, methods of measuring the electromotive force, effects of temperature and light upon the results, and means for eliminating or controlling polarizations. The final process was as follows: "Standardization" iron wires were sand-papered, wiped with filter-paper and covered all over with a coat of paraffine. When ready for use the paraffine was scraped from a short portion and the wire was wiped with filter-paper. The cell was made up with two glass beakers connected with cotton twine, the electrodes being clamped in insulating supports.

For measuring rapidly changing electromotive forces, the cell was connected to a mica condenser which could thus be charged and then discharged through a d'Arsonval galvanometer. The capacity of the condenser was adjusted so that the galvanometer read directly in volts, 10 cm. equal to 1 volt. Contact of the iron with the electrolyte was made by means of a movable platform, carrying the cell, mounted upon a lever with a counterpoise. The time from the instant of making the cell until the breaking of the condenser circuit was measured with a stop-watch.

For measuring slowly changing electromotive forces, a high resistance and a key were placed in series with the cell

and galvanometer, the resistance being such that the readings were the same as when used ballistically. The whole arrangement is shown in the accompanying diagram (Fig. 4).

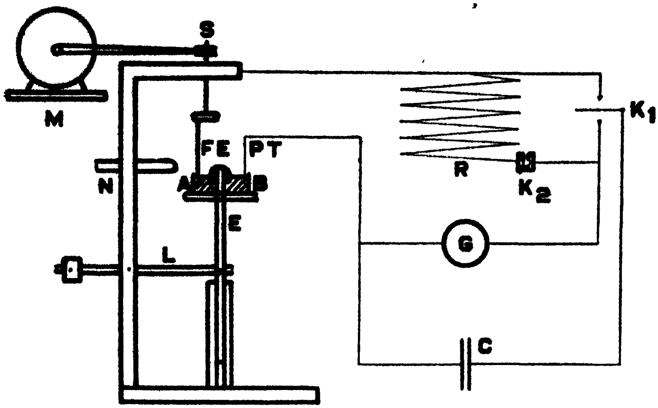

Fig. 4

A-B, Cell
C, Condenser
G, Galvanometer
R, Resistance
K_1, Charge and discharge key
K_2, Plug key
E, Movable platform
L, Lever and counterpoise
S, Spindle
M, Motor
N, Microscope
Fe, Iron
Pt, Platinum

The use of a small capacity, 2.586 M. F., and a high resistance, 832,000 ohms, practically eliminated all current, hence all changes in electromotive force are due to chemical changes independent of any electrolytic effects.

The results were obtained in two ways: first by starting with the iron at rest and then putting it in rotation after the electromotive force reached a steady value; second, by starting with the iron in rotation and then bringing it to rest after a steady electromotive force was reached. The results of the experiments in the two ways were similar, hence they will be recorded here as though they were obtained in the second way only. The following table gives the electromotive force of

the cell in volts at room temperature, 18–20 degrees, for the different density of acid.

TABLE II

Density	Electromotive Force in Volts					
	Active and Semi-passive			Passive		
	Iron in motion		At rest	Either at rest or in motion		
	Starting	Steady	Steady	Max.	Min.	Final
1.01	1.25	1.25	1.54	.50	.40	Active
1.09	1.23	1.23	1.35	.45	.25	.29
1.12	1.21	1.21	1.26	.40	.20	.28
1.17	1.19	1.19	1.20	—	—	—
—	—	—	1.18	.28	.18	.26
1.25	1.18	1.18	1.06	.26	.15	.24
1.32	1.16	.99	1.01	—	—	—
—	—	—	.95	.13	.10	.25
1.37	1.16	.89	—	—	—	—
—	—	.93	Passive	.12	.08	.26
1.41	1.13	.81	—	—	—	—
—	—	.84	—	—	—	—
—	—	Passive	Passive	.08	.03	.26

While this table gives only the starting, steady, maximum, minimum and final values of the electromotive force, many intermediate values were measured so that the whole change of electromotive force can be plotted against the time. This has been done in a slightly conventional way in Fig. 5.

No time scale has been placed upon the plot since different parts of the same curve are plotted on different time scales, and the length of horizontal parts, which represent steady states, are entirely without significance. The sloping parts of the curves represent gradually changing electromotive force; those represented in the upper parts of the curves take place in a few seconds, or minutes, while those in the lower parts require hours, days or even months.

The instant of bringing the iron to rest is marked with an R on each curve. The vertical lines indicate instantaneous changes in the electromotive force. In the 1.41 acid this instantaneous change takes place while the electrode is in

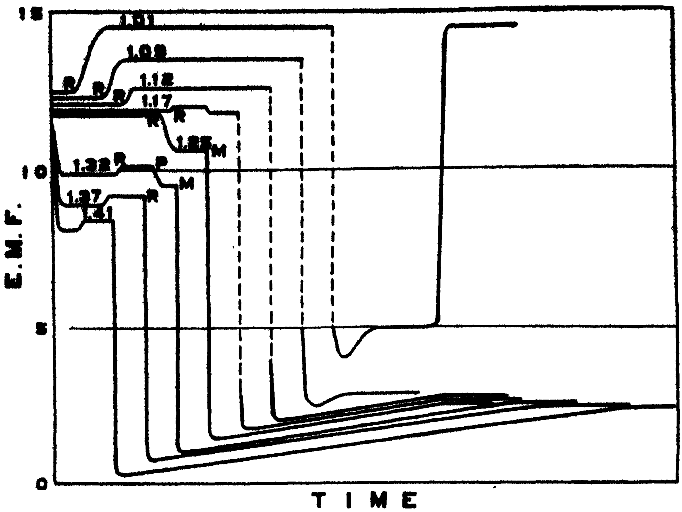

Fig. 5

motion. In the 1.37 acid it takes place as soon as the electrode is brought to rest. In the 1.32 and 1.25 acids it takes place if the iron is touched with mercury, silver, platinum or gold. This is indicated by M on the curves. In the more dilute acid this sudden change in electromotive force cannot be made to take place by touching with a metal, but if the iron is removed, dipped in concentrated acid, and then placed back in the dilute acid, the subsequent changes are similar to those which take place in concentrated acid. The broken lines indicate that this process was followed.

It will be noticed that in dilute acid up to 1.25 density, the electromotive force remains at the starting value as long as the electrode is kept in motion, and that the starting values are nearly the same in acid of all density, varying only from 1.13 volts in 1.41 density acid to 1.25 volts in 1.01 acid. Since the products of the chemical action are carried away by the motion of the electrode it can be inferred that the electromotive force results from the unpolarized electrode potential of ferrous iron in nitric acid. When the electrode potential was de-

termined for 1.01 acid by comparison with a calomel electrode it was found to equal + .10 volt. The slightly smaller values obtained in more concentrated acid are probably due to less complete dissociation. The electrode potential of iron in normal ferrous salts is given by Stieglitz,[12] as + .122, hence it can be inferred that ferrous ions are formed at the instant of making the cell in acid of all density.

No microscope observations are possible while the electrode is in rotation, but the surface of the electrode is bright in all dilute acid showing that in these acids the products are carried away as fast as they are formed. When the electrode is brought to rest the products of the reaction are carried away very slowly by convection currents and by diffusion, hence polarization takes place. As a result very marked changes of the electromotive force occur. In acids from 1.01 to 1.12 there is a rise to a maximum steady value in each case. That this rise is due to ferrous nitrate is shown by the fact that when a quantity of this salt is added to the dilute acid, the cell has an electromotive force of 1.5 volts from thestart, whether the electrode is in motion or at rest; while the addition of ammonium nitrate or ferric nitrate does not materially change the electromotive force of the cell. Moreover the microscope shows the green ferrous nitrate forming about the electrode and falling in a stream to the bottom of the cell where it slowly dissolves in the acid.

In the 1.17 acid the rise in electromotive force is very small and it is followed by a slight fall. The green liquid forms as in the more dilute acid but it quickly becomes brown and loses its color completely before reaching the bottom of the cell. This density is evidently a critical one in the process. As was seen above, this is the acid density at which ferrous nitrate ceases to be found as a final product of the reaction. The value of the electromotive force and the microscope observations show that the same reaction is taking place as in the more dilute solutions, but the oxidation of the ferrous nitrate to ferric nitrate takes place so rapidly that it has practically no

effect in raising the electromotive force of the cell when the electrode is brought to rest. There is evidently a balancing of the rate at which the ferrous nitrate is formed with the rate at which it is converted into ferric nitrate, the result being that the electromotive force is practically unchanged.

In the 1.25 acid there is a considerable fall in the electromotive force when the electrode is brought to rest. This is the acid density at which ammonium nitrate ceases to be formed and the nitric oxide as a final product reaches a maximum. It is also the density at which the so-called semi-passive state of iron first appears and it marks the "passive break" in the reaction velocity constant pointed out by Young and Hogg. Microscope observations show that as soon as the electrode is brought to rest a brown liquid film forms over the surface and within this film gas bubbles are formed. The liquid which streams from the electrode is practically colorless, being slightly green.

That the same ions are given to the solution here as in the more dilute acid is shown by the fact that the electromotive force is the same when the products are carried away. The fall in the electromotive force when the electrode is brought to rest must be due to a change in the reaction and the formation of a product which produces a polarization in the opposite direction from the ferrous nitrate. When the iron is removed in this condition it is found to be covered with a slimy liquid which rapidly forms crystalline plates over the surface of the iron.

In acid of greater density than 1.25 the drop in electromotive force takes place even while the electrode is in motion. This indicates that the film clings to the surface and is not removed by the motion.

When the iron is brought to rest in the 1.32 acid there is a slight increase in the electromotive force, probably due to the presence of some ferrous nitrate. This slight rise is followed by a considerable decrease. An examination of the iron when it is first brought to rest shows the presence of the brown liquid

and the formation of gas bubbles as in the 1.25 acid, but in this case the gas bubbles are formed at the surface and cling to the iron. A row of bubbles forms around the wire at the line where the paraffine joins the iron; a single bubble forms at the end of the wire; and more or less regular rows form over the surface of the wire. The activity is now greatest immediately under these bubbles. As a result of this local action the surface becomes pitted and the activity is confined to the bottom of the pits. During the formation of these pits the drop in electromotive force already mentioned takes place.

It is under these conditions that pulsations occur. (Marked P on the curve.) The pulsations consist of a kind of "geyser" action. The bubbles gradually increase in size and then the action suddenly stops, the bubbles being strongly repelled from the iron. The electrolyte now settles into the depressions and the action starts over again. At the instant of starting, the iron appears quite black. This action takes place simultaneously all over the surface, but at the line of separation between the iron and the paraffine the gas does not completely cease to flow. As a result of this continuous activity, the electrode is dissolved very rapidly along the line of separation and consequently is cut off long before the main body of the wire is dissolved. When such a piece is cut off it usually becomes passive over the whole surface immediately.

If the electrode is made several centimeters long only a few pulsations occur and then the whole surface becomes passive. When this happens the brown film quickly disappears and the iron has the silvery appearance characteristic of the passive state.

During the pulsating process the electromotive force drops to very low values at the instant of cessation of action and repelling of the bubbles, but no satisfactory measurements can be made since the period of cessation is so short. When the whole surface becomes passive the first electromotive force that can be measured is very small, but it continues to

decrease for some time when it reaches a minimum and then slowly increases to the final value which it maintains indefinitely.

In the 1.37 acid the process is similar to that in the 1.32 acid but no pulsations occur, the iron becoming passive as soon as it is brought to rest. In the 1.41 acid the iron becomes passive while it is kept in motion, but maintains a steady electromotive force for a short time in the semi-passive condition.

If iron which has been blued by heating in a gas flame is used as an electrode in any acid of greater density than 1.25, the electromotive force starts with the same value as when bright iron is used, but quickly goes to the low values without showing any indication whatever of an intermediate electromotive force. The presence of iron oxide apparently favors the production of the passive condition and prevents the formation of the semi-passive state. The oxide soon dissolves after the passive state is reached and the surface becomes bright.

The electrical action of the cell after the iron becomes passive is very similar in acid of all densities. Except in very dilute acid the final electromotive force is nearly the same in all cases, about .27 volt. The more concentrated the acid the smaller is the minimum value attained and the longer it takes to reach the final value.

An examination of the iron with a rather high power microscope shows that immediately after it becomes passive the surface becomes covered with very fine, transparent, needle-like crystals, and that a yellowish green liquid is formed among these crystals. No gas can be seen given off. Iron that has been passive for several weeks and has reached the final electromotive force shows no crystals and no trace of any liquid or gaseous film. The surface has the bright metallic luster of platinum.

If an electrode which has recently been made passive has the crystals rubbed off with filter-paper, and is then placed in concentrated acid, the electromotive force goes immediately

to the final value and then gradually drops to the minimum again. If an electrode which has reached the final condition is made active by touching with active iron in dilute acid and is then placed in concentrated acid, the electromotive force drops gradually to the minimum but soon returns to the final value.

These results seem to indicate that the drop in electromotive force below the final value is due to a polarization by the crystals, and that the final state is reached only after the crystals have dissolved. The chemical action which forms the crystals seems to be a last trace of activity, possibly by the iron just under the surface, after the general surface has become passive. This is indicated by the fact that the crystals seem to push out through small openings. In one case a single crystal was seen to push out fully a millimeter.

The very large, instantaneous drop in the electromotive force when the iron changes from the active to the passive state must be accompanied by a very marked change in the chemical reaction, involving a change in valence of the iron ion. It seems certain that there is a definite reaction between the passive iron and the nitric acid. Young and Hogg have shown that the rate of dissolution of passive iron is about one ten-thousandth of the rate for active iron. This means the same amount of passive iron dissolves in a week as of active iron in a minute. Pieces of passive iron wire have been kept in 1.25 acid for over a year, but all such pieces finally dissolved.

Theoretical

When these results are examined in connection with the chemical experiments enumerated above, a fairly complete notion can be obtained of the process taking place when iron acts upon nitric acid of different densities.

Iron unites with oxygen to form three oxides, one of which is commonly considered a combination of the other two. These oxides unite with water to form compounds which are amphoteric, i. e., which react with either acids or bases in the formation of salts. The oxides, together with the corre-

sponding hydroxides, are shown in the following diagram (Fig. 6), with their probable structural formulae. In order to indicate the amphoteric nature of the compounds, the ionization of the oxides has been indicated, as well as the ionization of water. The negative ion of the oxide and the positive ion of water constitute the acidic compound, while the positive ion of the oxide and the negative ion of water constitute the basic compound. Circles enclose the positive ion in every case.

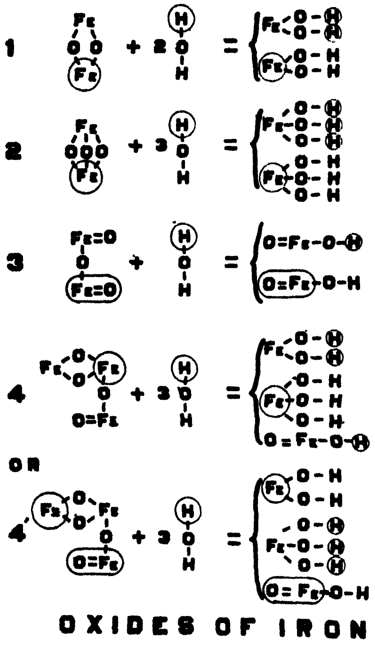

Fig. 6

1. Ferrous oxide + water = ferrous hydroxide
2. Ferric oxide + water = ferric hydroxide
3. Ferric oxide + water = meta ferric hydroxide
4. Ferroso-ferric oxide + water = { ferrous hydroxide; ferric hydroxide; meta-ferric hydroxide }

Since these compounds are weak bases or weak acids, the ionization of the oxide must be of the same order of magnitude

as the ionization of water and therefore the numbers of each of the ions must be of the same order of magnitude. It is this condition which makes the compounds amphoteric.

Any reaction which results in the formation of one of these oxides, or hydroxides, from another involves a change in the valence of the iron. Since increased oxygen necessitates increased valence and decreased oxygen necessitates decreased valence, such changes in valence are commonly termed oxiidations and reductions. The ease with which change of valence takes place and the tendency to form compounds with mixed valence are marked characteristic properties of iron.

Nitric acid is the strongest oxy-acid known. It results from the combination of nitrogen pentoxide with water, and thus stands at one end of a remarkable series of compounds of nitrogen, at the other end of which stands ammonium hydroxide. The structural formulae of some of these compounds and their ionization in combination with water are shown in Fig. 7.

In dilute aqueous solutions of nitric acid the hydrogen ion concentration is very large, hence the nitrate ion (NO_3^-) concentration must also be large. If we assume, as is usually done, that the dissociation of water is very slight, then the hydroxyl ion concentration must be very small.

When the concentration of nitric acid is increased, the hydrogen ion concentration falls off very rapidly as shown by its computation from hydrogen electrode potentials in solutions up to normal. This necessitates a corresponding decrease in the nitrate ion concentration and a considerable increase in the hydroxyl ion and nitro ion (NO_2^+) concentrations.

As a result of these changes, increased concentration of the nitric acid will ultimately result in a condition in which the order of magnitude of the numbers of each ion will be the same. When this condition is reached the acid must be considered weak and may be expected to act as an amphoteric solution.

Any reaction in the nitric acid which increases the hydrogen ion concentration furnishes the condition for reduction of the pentoxide of nitrogen to lower oxides. These oxides, when formed, may be thought of as dissociating and combining with water to form the lower compounds in the series as shown in the diagram. It is evident that in the most dilute acid such reduction may be expected to be the greatest, i. e., to ammonia, while in more concentrated acid the reduction will not proceed so far.

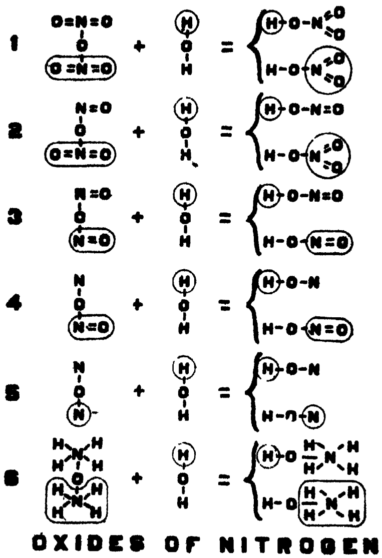

Fig. 7

1. Nitrogen pentoxide + water = nitric acid
2. Nitrogen peroxide + water = $\left\{\begin{array}{l}\text{nitrous acid}\\ \text{nitric acid}\end{array}\right.$
3. Nitrogen trioxide + water = nitrous acid
4. Nitric oxide + water = $\left\{\begin{array}{l}\text{hyponitrous acid}\\ \text{nitrous acid}\end{array}\right.$
5. Nitrous oxide + water = hyponitrous acid
6. Ammonium oxide + water = ammonium hydroxide

That a change such as is outlined above actually takes place in acid of increasing density, is indicated by a number of facts already mentioned. First, the conductivity, and hence the total ionization, begins to fall off in acid of 1.15 density; drops suddenly in acid of 1.35 density; and becomes extremely small in pure acid. Second, the reaction rate suddenly changes at a density of about 1.26. Third, electrolysis gives hydrogen and small amounts of nitrogen peroxide in acid below this density, but nitrogen peroxide and small amounts of hydrogen in acid above this density. Fourth, the reaction of dilute acid with iron gives only ferrous nitrate, its oxidation to ferric nitrate taking place more rapidly and more completely as the density of the acid increases. Fifth, ammonium nitrate is the principal reduction product with iron in dilute acid and its formation ceases when 1.26 acid is reached. Sixth, nitrogen peroxide is found in constantly increasing amount until it becomes the only reduction product in concentrated acid. Finally, the electromotive force of a cell with an iron anode starts with the same value in acid of all densities, but polarizations occur which constantly reduce the electromotive force as the density increases, the change from negative polarization to positive occurring in about 1.26 acid.

Assuming that double dissociation takes place as has been suggested, the action of iron on nitric acid may now be sketched in detail. Upon introducing iron into dilute acid, ferrous ions go into solution and the electrons thus liberated charge the iron negatively. If the charge is not removed a state of equilibrium will be established and the action will stop. There are two different positive ions, H^+ and $NO_2{}^+$, which may be attracted to the iron and by taking up electrons may become molecular and escape into the solution. When this occurs the charge on the iron will be reduced and the action will proceed. It is evident that hydrogen ions do not reduce the charge since no hydrogen is set free in acid of any density. Nitrogen peroxide is set free in small amount in dilute acid and constantly increases in amount as the density increases,

hence it is possible that it may reduce the charge. As will be seen below, it is quite probable that this does not happen except in concentrated acid.

There are two different negative ions with which the ferrous ions may unite, (NO_3) and (OH), hence two primary reactions are possible, thus,

(a) $Fe^{++} + 2(NO_3^-) = Fe\ (NO_3)_2$

(b) $Fe^{++} + 2(OH^-) = Fe\ (OH)_2$

Ferrous nitrate is formed in dilute acid and we know that nitrate ions are in excess, hence it is to be expected that the first reaction predominates, though there is nothing to preclude a limited amount of the second reaction. If ferrous hydroxide is formed, it undoubtedly reacts immediately with nitric acid to form ferrous nitrate, or it is oxidized as indicated below.

In order to account for the other products it will be necessary to assume varying amounts of reduction of the nitro ions by the hydrogen and ferrous ions; or, what amounts to the same thing, varying amounts of oxidation of hydrogen and ferrous ions by nitro ions.

There are three possible stages at which the oxidation of ferrous ions may take place. If ferrous nitrate has been formed and is oxidized to ferric nitrate, the process may be represented by the following equation:

$$Fe\ (NO_3)_2 + 2(NO_2^+) = Fe\ (NO_3)_3 + (NO^+)$$

This will reduce the valence of the nitrogen from 5 to 3, and increase the valence of the iron from 2 to 3. If ferrous hydroxide has been formed and is oxidized to ferric nitrate, the reaction may be the following:

$$Fe\ (OH)_2 + 4(NO_2^+) = Fe\ (NO_3)_3 + N^+ + H_2O$$

This will reduce the valence of nitrogen from 5 to 1. Finally, the oxidation may take place before the ferrous ion unites with a negative ion, in which case the nitro ion will take an electron from the ferrous ion and become molecular without a change in the valence of the nitrogen.

The reduction of the nitro ion by varying amounts of hydrogen ions is shown by the following equations:

$$
\begin{aligned}
&\text{(a)}\quad (NO_2{}^+) + 2H^+ = (NO)^+ + H_2O \\
&\text{(b)}\quad (NO_2{}^+) + 4H^+ = N^+ \quad + 2H_2O \\
&\text{(c)}\quad (NO_2{}^+) + 8H^+ = (NH_4{}^+) + 2H_2O
\end{aligned}
$$

The valence of the nitrogen is thus reduced from 5 to 3, 1, and -3. The positive ions thus formed may unite with negative ions; or they may be attracted to the iron and take up electrons, thus becoming molecular. One combination which takes place is evidently the union of $(NH_4{}^+)$ with $(NO_3{}^-)$ to form ammonium nitrate. The N^+ and NO^+ ions are attracted to the iron, where they are set free by reducing the charge. The nitrous oxide may be accounted for by assuming that N^+ ions unite with OH^- ions to form hyponitrous acid. This acid is known to be unstable and breaks down into nitrous oxide and water.

By comparing these assumptions with the results shown in Fig. 1, it will be seen that they fully account for the variations in the relative amounts of the different products and for the order in which they disappear.

The variation in the polarization of the cell is best accounted for by a gradual substitution of some product for the ferrous nitrate. According to the assumptions just made, the most probable product is ferrous hydroxide. There is considerable evidence that ferrous hydroxide is formed in acid of intermediate density. When the electrode is removed and rubbed between the fingers it has a slimy feeling, and the red or brown color which appears is characteristic of the formation of ferric salts from ferrous hydroxide. The formation of nitrogen in the film also agrees with this assumption.

It seems probable, therefore, that the semi-passive state is associated with the gradual change from the first primary reaction, which is acidic, to the second primary reaction, which is basic.

The final point to be considered is what happens when the

iron becomes passive. It is the writer's belief that the iron ceases to form ferrous ions, but forms ferric ions instead. It has been pointed out that although nitro ions are formed in dilute acid, they will be reduced by hydrogen ions and the ions which oxidize the iron will be NO^+ and N^+. When the acid is concentrated the hydrogen ion concentration will decrease and hence the reducing action upon the nitro ions will fall off. This will result in the solution finally becoming amphoteric and the basic reaction may predominate.

It seems reasonable to suppose that under these conditions the nitro ions actually react with iron to form ferric ions, thus:

$$Fe + 3(NO_2)^+ = Fe^{+++} + 3NO_2$$

Assuming that the basic reaction exists, the principal primary reaction would be the formation of ferric hydroxide, thus:

$$Fe^{+++} + 3(OH)^- = Fe\,(OH)_3$$

If the ferric hydroxide is dissolved in the acid the secondary reaction would be:

$$Fe\,(OH)_3 + 3HNO_3 = Fe\,(NO_3)_3 + 3H_2O$$

If the acidic reaction also took place, the equation would be:

$$Fe^{+++} + 3(NO_3)^- = Fe\,(NO_3)_3$$

Thus ferric nitrate and nitrogen peroxide would be the only products formed.

Nitrogen peroxide is a liquid at the temperature of the experiments and is readily absorbed by passive iron. This was shown directly by Young and Hogg. When iron which has been made passive in nitric acid is made active in the air, nitrogen peroxide is given off, as is shown by the formation of the brown fumes of nitric oxide.

The absorption of nitrogen peroxide and the existence of the passive state seem to be intimately connected and it is quite likely that the amount of oxide absorbed has much to do with the length of time that the iron remains passive when removed from the acid.

The evidence that passive iron gives off ferric ions seems quite conclusive. When the electrode of the voltaic cell be-

comes passive, the electromotive force drops instantly about one volt. Moreover, the final electromotive force is nearly the same in acid of all density, the variations being in the same direction and of the same magnitude as the variations in the starting electromotive force. Such a result as this cannot be due to a polarization, for in that case the change would be gradual and much smaller. The electrode potential of passive iron in nitric acid is —.88 volt. P. F. Hammond,[13] in his paper, "The Influence of the Metallic Ions upon the Electric Potential of a Metal Placed in the Solution," gives the electrode potential of the ferric ion as —.94 volt. This agreement indicates strongly that passive iron is ferric.

The theory that the active state of iron is ferrous and the passive state ferric is usually attributed to Finkelstein.[14] He was led to this suggestion by the change in the electrode potential of iron in mixed ferrous and ferric chloride solutions as the relative amount of the salts varied. He considered ordinary iron to be a mixture of ferrous and ferric, while passive ferric iron was considered to be a noble form of the metal produced by a process of oxidation in the passivifying liquid.

Ordinary contact electromotive force measurements place iron near tin in the Volta series, and ordinary electrolytic measurements place iron near tin in the electrode potential series. This would make it appear that ordinary iron is ferrous. Sanford[15] has pointed out, however, that the properties of iron which are determined by its cohesion would place it near platinum in the Volta series, and he has shown experimentally that when passive iron is used in contact potential experiments it is strongly electronegative.[16]

Many of the chemical properties of iron indicate that it is far more like platinum than like tin.

Hence, there is good reason for supposing that ordinary iron is essentially ferric; that it is a noble metal. In that case the reason that ordinary electrical experiments make iron appear as ferrous must be that the conditions surrounding the surface are such that only ferrous ions are formed. From

this standpoint it would be more proper to speak of active iron as "debased" than of passive iron as "ennobled."

That iron acts as divalent under ordinary conditions while it is essentially trivalent does not seem at all improbable. Valence is undoubtedly an electrical condition determined by the absence or presence of electrons in the ions formed. Iron is characterized by having three electrons which may be given up when it forms ions. Under some conditions it gives up only two of these electrons and forms divalent ions, whereas under other conditions it gives up all three electrons and forms trivalent ions. The only peculiarity is that the conditions for the first process are common, while those for the second are rare, and only occasionally, as in the case of nitric acid, the conditions for both processes exist in the same solution.

If these conclusions are correct, it would seem that they should apply to other metals which form double series of salts which readily change from one to the other. The other metals which are known to show both the active and passive states in nitric acid are chromiüm, cobalt, tin, nickel and lead, and these all possess this property.

It would seem also that other solutions which possess the characteristics of both acids and bases should show both states of certain metals. The action of iron has already been studied by the above methods in hydrochloric acid, sulphuric acid, chromic acid and potassium dichromate. Ordinary concentrated hydrochloric and sulphuric acids showed no tendency to form both states, while chromic acid and potassium dichromate gave results similar to nitric acid.

It is well known that iron becomes passive if made the anode of certain electrolytic cells, when a certain density of current is maintained. The necessary density of current increases as the dilution of the solution increases. It would seem that when the electrons are carried away from the iron fast enough the electrolyte may furnish the conditions which cause the formation of ferric ions when it otherwise would not. It

may be considered that the current carries the hydrogen ions to the cathode, while the hydroxyl ions are carried to the anode. This reduces the acidic character of the electrolyte about the anode and increases its basic character, with the result that the basic reaction takes place and the iron begins to form ferric ions.

Stated in simple form, the theory is that iron is essentially ferric; that it forms ferric ions in bases and weak acids where the reaction is very slow; but it forms ferrous ions in strong acids where the reaction is very rapid.

There is a possibility that iron gives off both ferrous and ferric ions in the active state. The action in nitric acid could be accounted for on this assumption quite as well as on the assumption that only ferrous ions are formed. This is a subject for further investigation.

It is believed that the principles involved in this theory are of general application. It seems probable that elements which form weak acids or weak bases possess atomic structures such that slight variations in the physical conditions will cause them to change their valence and even their sign with reference to the components of water. The loss or gain of a single electron might affect the electrical condition very greatly or very slightly depending upon the number of electrons involved and their positions in the atom.

The position of the elements in the contact potential series or electrode potential series must depend in part upon the valence and sign of the ions which are formed under the conditions used for comparison. The ordinary condition under which comparisons are made is in the presence of water at ordinary temperatures. An entirely different set of conditions might result in different positions for some of the elements. Certain elements form extremely stable compounds with water and hence slight changes in physical conditions would not be likely to change their ionization. Other elements form very unstable compounds with water and their ionization would be likely to change with slight variations in the physical

conditions. Potassium is an example of the first class while chromium is an example of the second class.

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THE ACCLIMATIZATION OF YEAST TO AMMONIUM FLUORIDE AND ITS REVERSION IN WORT

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Addition of 0.4 decigram of hydrofluoric acid per litre (calc. as HF) to wort, while not injurious to yeast, kills bacteria and the lactic acid ferment and thus increases the yield of alcohol;[1] up to 0.15 decigram per litre are used in the manufacture of alcohol from beets[2] but a larger quantity is harmful to the fermentation. Klöcker[3] points out that the use of this substance is advisable only in distilleries, and Sykes[4] advises against its use in breweries, possibly because it seems to encourage the growth of wild yeasts.

Effront[5] found that in wort containing 3.0 decigrams of ammonium fluoride per litre yeast "seemed completely to lose its activity" but that if transferred to fluoride-free wort "it immediately recovered its fermentative power, and showed an extraordinary power of reproduction." He also discovered that by planting yeast in wort containing 0.2 decigram of ammonium fluoride per litre and repeatedly transferring it to higher concentrations of fluoride, he could obtain cells which caused active fermentation in wort containing 3.0 decigrams per litre: "The yeast had become accustomed, so to speak, to the antiseptic and had acquired a certain immunity which it did not possess originally." Effront's experiments were continued by Sorel[6] who finally got his yeast to grow in wort containing 10 decigrams of hydrogen fluoride per litre, which corresponds to 18.5 decigrams of the ammonium salt.

In the present paper are recorded the results of experiments on: I, the toxicity of concentrated fluoride solutions, with

[1] Sorel: Comptes rendus, **117**, 253 (1894).
[2] McIntosh: "Industrial Alcohol."
[3] Klöcker: "Fermentation Organisms."
[4] Sykes: "Principles of Brewing."
[5] Effront: Comptes rendus, **118**, 559 (1893).
[6] Sorel: Loc. cit.

and without alcohol; II, the delay in reproduction in wort containing fluoride; III, the effect of fluoride concentration on the delay; IV, the difference in behaviour towards ammonium fluoride of yeast acclimatized by different methods; V, the maximum concentration of fluoride in which yeast will reproduce; VI, the reversion of acclimatized yeast to normal when grown in fluoride-free wort; VII, the evidence of selection; and VIII, the evidence of adaptation during the process of acclimatization.

I. Toxicity of Ammonium Fluoride towards Yeast

The experiments were carried out in a rocker tube[1] at 25° C. with "normal yeast"[2] in a five percent aqueous solution of ammonium fluoride.

TABLE I

Time in poison	0	27	32	45	minutes
5% amm. fluor.	800	250	50	1	colonies on agar
Killed	0	68	93	100	percent

In a second series, the action of 4.8% ammonium fluoride in water was compared with that of 4.8% ammonium fluoride and 2.5% ethyl alcohol. (By % is meant grams per 100 cc of solution.)

TABLE II

Time in poison	0	10	13	17	23	28	38	minutes
Aqueous sol'n	77	30	—	23	16	4	1	colonies
ditto killed	0	60	—	70	80	95	100	percent
Alcoholic killed	—	—	100	100	100	100	100	percent

Similar experiments were carried out using solutions of ammonium fluoride to which a little methylene blue had been added; a purple precipitate is formed, and but few of the cells stain; a series was run with phenol to control the yeast.

[1] Fraser: Jour. Phys. Chem., **25**, 4 (1921).

[2] Fulmer: Ibid., **25**, 12 (1921).

TABLE III

Time in poison	5	6	8	9	20	26	minutes
0.658% ph. + MB	25	40	—	65	—	—	% stained
5% Am. fl. + MB	0	—	2	—	—	7	% stained
10% "	—	—	—	—	7	—	% stained
20% "	—	—	—	—	—	10	% stained

In another series, yeast was shaken in the rocker with ammonium fluoride solution, filtered off, and washed, before adding the MB; with 4%, 6%, and 8% ammonium fluoride not over 20% of the cells were stained in half an hour; and after 20 minutes in 20% ammonium fluoride solution only half the cells were stainable.

II. Delayed Fermentation

On repeating Effront's experiments it was found an easy matter to acclimatize yeast to ammonium fluoride in wort by the "stepping up" process employed by him; it soon appeared, however, that it is quite unnecessary to begin with a low concentration of fluoride; the cells can be planted at once in solutions of high concentration and will grow *provided they are left long enough.*

In the experiments, 50 cc wort was pipetted into a 250 cc Erlenmeyer flask, which was stopped with cotton wool and sterilized for 30 minutes in live steam at 100° C, where it loses 0.25 g by evaporation. After cooling, a small accurately measured volume of 24.07% ammonium fluoride solution was added, then enough water to bring the whole to 51.2 cc and finally the 1.0 cc of suspension of yeast in water count 150. The total volume was thus 52.2 cc, and if 0.218 cc fluoride solution had been added, the concentration would be 10 dg per litre; the "count" of yeast would be 3. The flasks were then let stand in the incubator at 25° C, and the time determined which elapsed between the addition of yeast and the appearance of flecks of foam on the surface.[1] Sykes[2] states that the "head" forms from 2 to 3 hours after carbon dioxide

[1] Fulmer: Jour. Phys. Chem., **25**, 10 (1921).
[2] Sykes: "Principles of Brewing."

is first given off; this was corroborated by the use of fermentation tubes. Whatever the concentration of the fluoride the number of cells per cubic centimeter of the medium when flecks first appear is about 50 x 250,000; the data in the following table were obtained at widely different times, with different yeasts and different worts; the count[1] was made in every case within half an hour of the first appearance of the flecks.

TABLE IV

Ammon. fluor.	0	10	10	10	10	20	20	20	20	30	40	dg per l.
Count	74	64	57	49	52	53	49	56	30	47	40	(av. 51)

The interval between seeding and fleck formation depends on the concentration of the fluoride; but it depends also on the way the wort has been prepared, and on the nature of the yeast used.

Variation in the Wort.—The standard method of preparing the wort was to digest 360 g coarsely ground brewer's malt with 1150 cc distilled water for 24 hours at 55° C, filter through toweling and paper, and sterilize for settling for 15 or 20 minutes in an autoclave with steam at 15 lbs. After three days, it was filtered again and used undiluted. Its specific gravity was 1.07; 100 cc contained 16.2 g dry matter including 0.412 g ash, of which 0.023 g CaO and 0.017 g MgO. If the temperature of digestion rose to 65–70° C, the wort seemed as good as ever for the purpose of growing yeast, but ammonium fluoride added to such a wort in quantities up to 40 decigrams per litre had no effect on yeast; such wort has a higher density, its ash was not determined. The time of digestion at 55° C also affected the wort. A considerable precipitate is formed when ammonium fluoride is added to wort, but filtration had no effect on the time elapsing before active fermentation. Neither had the time (0 to 192 hours) which might elapse between adding the fluoride to the wort and inoculating with yeast. If, however, the wort be ster-

[1] Fraser: Jour. Phys. Chem., **25**, 3 (1921).

ilized after the fluoride has been added, the effect of the fluoride is much reduced.

Variations in the Yeast.—As already observed by Sorel, yeast which has grown in wort containing fluoride is apt to form large clusters, more like bunches of grapes than like the ordinary chains. Similar bunches, though smaller, may sometimes be obtained from the colonies on a plate made direct from a Fleischmann's yeast-cake. Ten flasks of fluoride-free wort were inoculated from different colonies of the same plate and were left to ferment; in one of them (No. 806) the yeast was very thickly bunched with but few single cells; in a second (No.804) there were many bunches but also a large number of chains; in a third (No. 808) there were some clusters but more double and single cells; the other seven were normal. Yeast from these ten cultures was planted in wort containing 10 decigrams of ammonium fluoride per litre, and the interval to fleck formation determined for each; the results showed that the greater the bunching, the shorter the interval.

TABLE V

Culture number	806	804	808	the 7 others
Flecks formed in	50	57	73	81 to 107 hours

This result was confirmed by another experiment for which a culture was selected because of its freedom from long chains or bunches of any kind; in this case 122 hours elapsed before the flecks appeared. That growth for long periods in (daily renewed) fluoride-free wort may increase the susceptibility of yeast to ammonium fluoride is shown by the data given in Table XII.

III. Influence of Fluoride Concentration on the Delay

That the time elapsing between seeding and fleck formation may be represented by a simple exponential function of the fluoride concentration is shown by the following results. (50 cc wort in flasks at 25° C; initial count 3; "conc. 40" means 40 decigrams of ammonium fluoride per litre of medium; it is in hours.)

TABLE VI

Conc.	0	3	6	9	12	13	20	25	30	35	40
t obs.	12	13	15	40	46	64	89	136	188	240	400
t calc.	(21	26	32)	40	50	63	91	132	190	275	400

The numbers after "t calc." are from the equation $\log_{10} t = 1.312 + 0.03225$ conc.

This relation has been verified repeatedly with various worts and yeasts, and though the constants of the equation vary considerably with these factors, yet the graph (log t against conc.) always gives a fairly straight line when the concentration lies between 10 and 45 decigrams per litre.

It being thus possible to acclimatize yeast to a high concentration of fluoride either by "stepping up" (Effront and Sorel's method) or directly, it seemed of interest to ascertain whether the method employed had any influence on the behaviour of the acclimatized yeast towards still higher concentrations of fluoride.

IV. Comparisons of Yeast Acclimatized by Different Methods

For this purpose two series of experiments were undertaken. In the first yeasts A to H were used, and in the second yeasts J to R. Yeast A was from a "normal" culture in pure wort; yeast B was taken from a solution containing 12 dg ammonium fluoride per litre which had been seeded with yeast A and let come to active fermentation; this life history may be synopsized by writing 0-12 after B. Yeast C (0-20) was from a solution of concentration 20 seeded with A. Yeast D (0-20-25) was from an actively fermenting sort containing 25 decigrams of fluoride per litre, which had been seeded with C; and similarly with the others. Each of these yeasts was used to seed a number of flasks of wort containing fluoride in various concentrations; the interval between seeding and fleck formation (in hours) for each case is given in the horizontal line which begins with the symbol identifying the yeast. The data from the second series are given in Table VIII; they started from a different "normal" yeast (Yeast J).

TABLE VII

Conc. of fluoride	15	20	25	30	35	40	45	50	55
A* (0)	64	89C	136	188	240	400	—	—	—
B (0-12)	17	17	66	—	—	—	—	—	—
C* (0-20)	—	43	48D	90	156	—	—	—	—
D* (0-20-25)	—	—	16	20	27E	60	—	—	—
E* (0-20-25-40)	—	—	—	—	16	20F	48	152	—
F (0-20-25-35-40)	—	—	—	—	—	20	48G	152	400
G (0-20-25-35-40-45)	—	—	—	—	—	—	96H	112	192
H (0-20-25-35-40-45-45)	16	16	—	—	—	72	90	97	—

TABLE VIII

Conc. of fluoride	10	15	20N	25	30	35	40	45
J* (0)	80L	106Q	180	159K	187	211	—	—
K* (0-25)	—	—	15	20	26	44	68	112
L* (0-10)	38	48M	66	134	112	168	—	—
M (0-10-15)	—	—	36	—	—	—	—	—
N (0-10-15-20)	—	—	—	16P	—	—	—	—
P* (0-10--15-20-25)	—	—	—	14	17	27	44	68
Q (0-15)	—	—	—	133R	—	—	—	—
R* (0-15-25)	—	—	—	42	59	86	112	136

These results show clearly that the "delay" is much less when the yeast used for seeding had previously been grown in a fluoride solution. Comparing Yeast G with Yeast H, it seems that a second period in concentration 45 somewhat further reduces the delay; acclimatization was evidently not quite completed in the first flask. Yeasts K, P and R, which had been acclimatized to concentration 25 by different routes, show considerable differences in their behaviour; P, which had lived longest in fluoride solutions, showed the least delay, but K showed less than R; no doubt the results are influenced to some extent by factors as yet undiscovered.

V. Maximum Concentration of Fluoride

Some of the results (those indicated by asterisks in Tables VII and VIII) are plotted in Figs 1 and 2. Omitting the experiments where the concentration of ammonium fluoride was lower than that in which the yeast had already been living, the others fall fairly well on straight lines converging to a point at concentration 80 in the first case and 72 in the second. If this

extrapolation were to be taken seriously, it would indicate that for concentrations above 80 decigrams ammonium fluoride per litre yeast already accustomed to fluoride would take longer to cause fermentation than would unacclimatized yeast. Attempts were made to grow yeast in these high concentrations. On May 1st, 1917, a number of solutions were seeded to a count of 3 with yeast grown in wort containing 36 dg fluoride per litre; on October 1st, five months later, the flasks were examined with the following results:

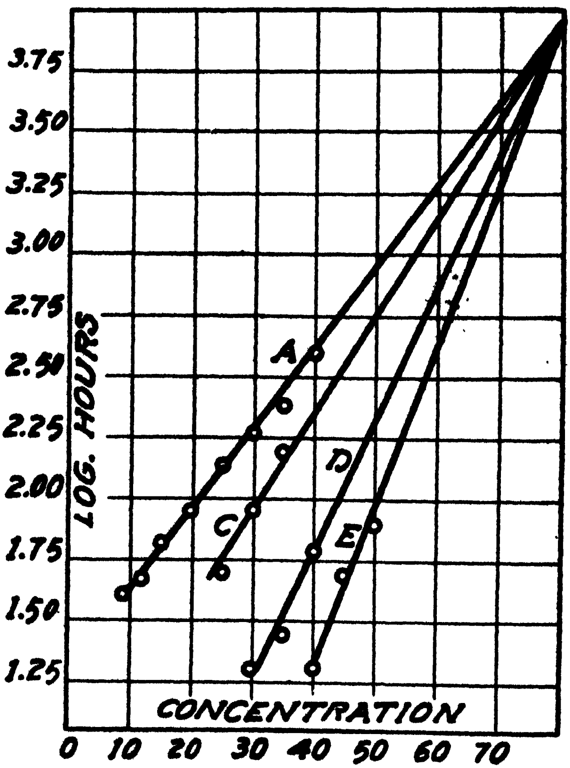

Fig. 1

TABLE IX

Conc.	0	36	50	65	80	dg per litre
Count	2000	4	320	3	3	

according to this, the highest concentration in which the yeast would grow lies between 65 and 80. A "normal" yeast from fluoride-free wort was then seeded into worts containing fluoride of the concentrations 65, 70, 75, 80 and 85 dg per litre; there was active fermentation in 65 after 760 hours, and in 70 after 1000 hours, the others were kept for four months without fermentation occurring. These results show that the highest concentration in which active fermentation will occur is about the same for the two yeasts, one acclimatized and the

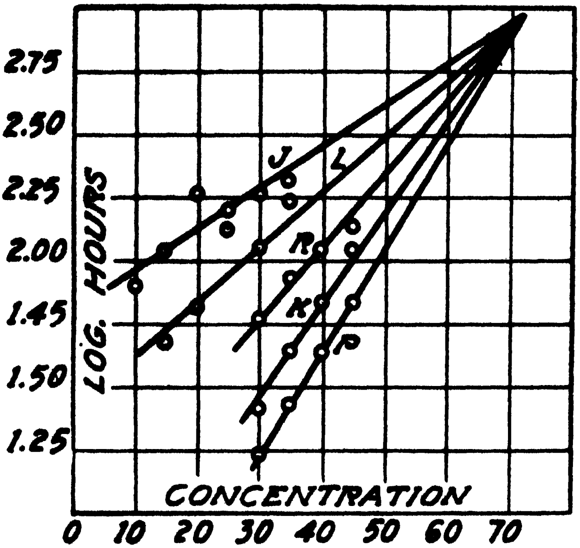

Fig. 2

other not; and that it lies close to 70 decigrams of ammonium fluoride per litre, that is, just below the crossing-points of the lines on the two graphs (Figs. 1 and 2). The "absurd" relations predicted for higher concentrations are thus unrealizable.

VI. Behaviour of the Acclimatized Yeast towards Phenol

To see whether the resistance towards fluorides, and the physiological changes noted by Effront and Sorel are accompanied by change of behaviour towards other reagents, yeast that had been grown in wort containing 30 dg ammonium fluoride per litre was used to seed wort containing 20 dg per litre, and when active fermentation took place (22 hours after seeding) the culture (*Y 20-30*) was compared with a normal culture (*Y 0*) from fluoride-free wort, with the following results (rocker, 25° C, 0.650% phenol in aqueous solution):

TABLE X

Tube 1 Y(0), phenol MB		Tube 2 Y(30-20) phen. MB		Tube 3 Y(0) phenol Plating		Tube 4 Y(20-30) Plating	
Min.	% std.	Min.	% std.	Min.	% killed	Min.	% killed
3	3	11	33	9	100	10	35
12	98	17	39			15	90
18	100	25	31			22	92
		40	34				

Whether ability to stain or inability to form colonies on wort agar be taken as criterion of death, yeast grown in fluoride solutions is more resistant to phenol than the other.

VII. Reversion

Plates.—Yeast was seeded from fluoride-free wort into wort containing 12 decigrams of ammonium fluoride per litre; when active fermentation occurred the culture was used to seed wort containing 25 decigrams of ammonium fluoride per litre, and so on, as follows; the concentrations are given in parentheses, and the intervals in hours between seeding and fleck formation are printed between them:

(0)-46-(12)-66-(25)-17-(30)-16-(30)-16-(30)

The delay when seeded into concentration 12 shows that the yeast used was similar to yeast A of Tables VI and VII.

From the last flask a wort-agar plate was seeded; three days later, four colonies on this plate were used to seed four flasks of wort; and when active fermentation was in progress

the cultures were used to seed (to a count of 3) four flasks of wort containing 30 decigrams of ammonium fluoride per litre. Flecks were formed 44, 48, 39, and 48 hours after seeding. As Yeast A required 188 hours, the yeast experimented with had obviously not lost all its acquired resistance by three days' growth on the plate followed by one transfer through fluoride-free wort.

Twelve days after the plate had been seeded, portions of two of the colonies already used were treated as before; the interval between seeding and fleck formation in this case was found to be 120 and 144 hours; so that even after twelve days' growth in the absence of fluoride the reversion was not complete.

Flasks.—Another yeast, taken from a wort containing 30 decigrams of ammonium fluoride per litre, was used to seed fluoride-free wort; every 24 hours a fresh flask of the same wort was seeded from the previous flask to a concentration of 2 or 3, thus the yeast was kept continually active. At intervals this culture was used to seed wort containing 30 decigrams of ammonium fluoride per litre (in duplicate) and the interval to fleck formation was determined, and is given after "delay" in Table XI.

TABLE XI

Hours in wort	0	23	48	71	95	117	140	165	189
Delay (1st flask)	38	42	65	70	90	117	140	144	170
Delay (2d flask)	41	47	65	72	90	125	140	144	170

When graphed (delay, hours in wort) these numbers fall not far from a straight line; in spite of the long delay of 170 hours in the last experiment, it would seem that the reversion was not complete after 189 hours in fluoride-free wort. The cells were still noticeably bunched, which points to the same conclusion.

Comparative experiments in which a normal yeast was grown in wort (under the same conditions of replanting) for 480 hours, and then used to seed fluoride worts of various

concentrations, showed that the "delay" in every case was greater than with the original yeast.

TABLE XII

Conc.	10	15	20	25	30	35	40	dg per l
Normal yeast	43	82	82	127	206	—	228	hours
After 480 hours	64	105	151	182	—	—	387	hours

In view of these results there is no way of predicting the degree of delay that would signify complete reversion.

VIII. Selection

When the foregoing experiments had established beyond all question that addition of ammonium fluoride to wort increased the interval between seeding (to count 3) and the appearance of flecks (count 50), the first explanation to suggest itself was that the fluoride may kill nearly all the 25 to 35 million cells (count of 3 in 50 cc wort) seeded into the flask, and that the extra time is needed for the remaining few to reproduce to a count of 50. Effront's "acquisition" of immunity would thus be reduced to a case of survival of the fittest, the process being "selection" by the poison; the experiments cited above under "variation of the yeast," which show that different cells from the same cake, and even different descendants of the same yeast-cell, may behave very differently towards ammonium fluoride, lend support to this view.

To test it, worts containing 9, 12, and 15 dg ammonium fluoride per litre, respectively, were seeded with yeast, and at noted intervals portions were removed, diluted, counted, mixed with wort agar, and poured into petri dishes. The following are the results obtained; time is measured in hours from the moment of seeding; duplicate plates were poured in each case and the number of colonies added; "active" means active fermentation in the flask; the experiments of each table were carried out at the same time with the same yeast, but the yeasts were not the same for the three tables.

TABLE XIII

Conc. Hours	9 Colonies	12 Colonies	15 Colonies
0	600 + 600 = 1200	600 + 600 = 1200	600 + 600 = 1200
1	20 + 24 = 44	20 + 24 = 44	27 + 24 = 51
16	10 + 14 = 24	0 + 0 = 0	0 + 0 = 0
23	25 + 26 = 51	3 + 2 = 5	0 + 0 = 0
41	active	352 + 370 = 723	33 + 34 = 67
45	——	active	slightly active

TABLE XIV

Conc. Hours	9 Colonies	12 Colonies	15 Colonies
0	600 + 650 = 1250	600 + 650 = 1250	600 + 650 = 1250
1	67 + 80 = 147	26 + 21 = 47	35 + 34 = 59
11.5	4 + 3 = 7	0 + 1 = 1	0 + 1 = 1
16.5	24 + 14 = 38	4 + 1 = 5	5 + 3 = 8
20.5	43 + 50 = 93	2 + 1 = 3	4 + 0 = 4
35	active	slightly active	4 + 3 = 7
40.5			35 + 40 = 75
45			active

TABLE XV

Conc. Hours	9 Colonies	12 Colonies	15 Colonies
0	313 + 335 = 648	300 + 300 = 600	250 + 300 = 550
16	50 + 35 = 85	31 + 32 = 63	35 + 32 = 67
23	11 + 6 = 17	0 + 1 = 1	2 + 2 = 4
39	active	28 + 28 = 56	24 + 24 = 48
46		38 + 45 = 83	25 + 50 = 75
61		active	active

If inability to form colonies on wort agar be regarded as evidence of death—the plates were kept at 25° C for a week to allow time for growth—it is clear that the fluoride kills a large proportion of the cells, and the proportion killed seems to increase with increase in the concentration of the fluoride. In Table XIII, for instance, not one cell in 1200 remained alive after 16 hours in wort containing 15 decigrams of ammonium

fluoride per litre. Whatever else it may do, the fluoride certainly acts as a selective agent.

IX. Adaption

To see whether anything beside selection is at work, measurements of the rate of reproduction of yeast were undertaken; the number of cells in the culture being counted at intervals by means of a haemocytometer.[1]

In a uniform medium, with plenty of food and the cells not too closely crowded, it is natural to expect that each cell would grow independently of the others, and that therefore the rate of increase of the number of cells in the flask at any moment would be proportional to the number of cells then present in the flask, i. e. (writing C for the "count"), $dC = k'C.\,dt$, whence $\log_{10}\frac{C_2}{C_1} = k(t_2 - t_1)$ where $k = 0.434\ k'$. If this assumption were true, the plot of log $\log_{10}$ C against t would be a straight line.

According to Euler[2] this formula was first proposed by Basenau[3] in 1895. Euler himself employed it in recording his experiments on the growth of yeast in media containing lactose, and if he had thought to omit the first point $(t = 0)$ he would have obtained fairly straight lines—this neglect could be justified because of the probability that some of the cells with which he inoculated the lactose were unable to reproduce in that medium. Slator[4] and Carlson[5] have also employed this formula in their work on yeast.

My own measurements were made to see how closely this formula will enable one to calculate the initial count by extrapolation from counts made after many hours of growth. The results of four such experiments are here recorded in full; all were made with 50 cc fluoride-free wort in Erlenmeyers at 25° C.

[1] Fraser· Jour. Phys. Chem., **25**, 3 (1921).
[2] Zeit. physiol Chem., **81**, 58 (1912).
[3] Chem. Centralblatt, **1895**, **I.**
[4] Biochem. Jour., **7**, 197 (1913).
[5] Biochem. Zeit., **57**, 313 (1913).

TABLE XVI

t	0	6.5	15.5	19.5	23	39.5	hours
C	(2)	13	100	275	350	300	
log C	0.30)	1.11	2.00	2.44	2.54	2.78	

TABLE XVII

t	0	15.25	17.0	18.75	hours
log C	(0.00)	2.16	2.45	2.60	

TABLE XVIII

t	0	16.25	18.25	19.0	20.0	21.0	22.0 hours
log C	−(0.30)	2.36	2.60	2.75	2.88	2.83	3.00

TABLE XIX

t	0	21.0	23.0	24.0	hours
log C	(−4.0)	0.96	1.34	1.56	

Plotting these numbers (log C against t), but omitting the point for $t = 0$, it is obvious that the best line for Table XVI runs through $t = 6.5$ and $t = 19.5$; from these two values there follows for $t = 0$, $C = 2.8$, whereas the initial count in the actual experiment was 2.0. From Table XVII, $t = 15.25$ and $t = 18.75$ give by extrapolation an initial value $C = 1.6$, as against 1.0 actual. For Table XVIII, $t = 16.25$ and $t = 20$ give 1.4, the actual value was 0.5; and for Table XIX, $t = 21$ and $t = 24$ give 0.0006 instead of 0.0001. Nine series of this kind were carried out, with different yeasts and different worts; in all of them the extrapolated values of the initial concentration were higher than the true values, the ratio varying from 1 to 8; the method therefore can be relied upon to give at least the order of magnitude of the number of cells originally present in the solution.

Similar measurements with worts containing ammonium fluoride were then undertaken; for the present purpose it is sufficient to quote the results of one of them where the wort contained 40 dg ammonium fluoride per litre:

TABLE XX

t	402.5	403.5	405.5	407.5	hours
log C	1.80	1.90	2.02	2.14	

The graph gives a fairly straight line from which can be calculated k = 0.064 (about half the value with pure wort), and for t = 0, C = 10^{-24}, or 1.25 x 10^{-15} cells in the 50 cc. A similar experiment with another yeast in the same concentration gave 10^{-23} and a number of others with various concentrations of fluoride led to analogous results. As at least one cell must have been left alive to cause fermentation and reproduction, these extremely low values decisively negative the hypothesis that all but a few of the cells were killed by the fluoride and that these few reproduced regularly from the beginning. They show that in addition to a selective action the fluoride must have caused something analogous to paralysis in the cells left alive; on recovery they possessed the power to reproduce in the fluoride solution at about half the rate of normal cells in pure wort. This modification of the properties of the cells is what constitutes "adaptation;" so that adaptation as well as selection plays a part in the development of a fluoride-resisting yeast.

It seemed at first that a rough idea of the duration of the paralysis might be obtained by subtracting from the total interval between seeding and fleck formation, the time estimated to be needed for the yeast to increase in number to a count of 50; for normal yeast seeded to a count of 2 or 3 in fluoride-free wort, this is about 12 hours, probably longer in the presence of fluorides. If then 12 hours be subtracted from the total period, the remainder will certainly give a maximum value for the duration of paralysis, even though the calculation seems to involve the improbable assumption that recovery is instantaneous. The data of Table VII give means of calculating the maximum duration of paralysis when "Y 25" (i. e., a yeast that will actively ferment wort containing 25 decigrams of ammonium fluoride per litre) is evolved from normal yeast, either directly (136 — 12 = 124 hours), through

concentration 12 (46 + 66 — 24 = 88 hours) or through concentration 20 (89 + 48 — 24 = 113 hours); in the case of Y 40, the times are: direct (400 — 12 = 388 hours), through concentrations 20 and 25 (89 + 48 + 60 — 36 = 161 hours), or through concentrations 20, 25, and 35 (89 + 48 + 27 + 20 — 48 = 136 hours). Such calculations, however, only give the maximum values; either the total period of paralysis is shorter when the concentration is increased by steps, or a very much larger proportion of the cells are killed outright when concentrated fluoride acts on unadapted yeast; without further data it is impossible to decide; the figures of Tables XIII, XIV, and XV, however, show that a good deal of weight must be attached to the second factor.

These experiments were carried out in the chemical laboratory of the University of Toronto in the winters of 1917–1919 under the direction of Professor W. Lash Miller; my thanks are due to Mr. N. A. Clark for help with some of the later measurements.

Summary

(1) The toxicity towards yeast of a few aqueous and aqueous-alcoholic solutions of ammonium fluoride has been determined; alcohol increases the toxicity.

(2) In acclimatizing yeast to ammonium fluoride it is not necessary to begin with low concentrations (Effront's stepping-up method), the cells may be planted at once in the more concentrated solutions of fluoride and wort, and will grow if left long enough.

(3) The time elapsing between seeding and active fermentation depends on the method of preparing the wort, on the character of individual yeast cells, and on the previous history of the culture.

(4) Yeasts acclimatized to a given concentration of fluoride by different routes behave differently towards more concentrated fluoride solutions.

(5) If the logarithm of the interval (see III above) be plot-

ted against concentration, for various yeasts, acclimatized and unacclimatized, the experimental data fall on straight lines radiating from a point corresponding to about 70 or 80 decigrams of ammonium fluoride per litre.

The highest concentration in which yeast will grow is about seven grams ammonium fluoride per litre; the highest reached by Effront was about 0.3 g per litre; Sorel reached 1.0 g hydrogen fluoride per litre (corresponding to 1.8 g ammonium salt).

(6) Yeast acclimatized to ammonium fluoride is more resistant to phenol than is normal yeast.

(7) Acclimatized yeast may be grown on fluoride-free wort agar for 12 days, or in fluoride-free wort for 190 hours without completely reverting to normal.

(8) When yeast is planted in wort containing ammonium fluoride, a proportion of the cells die, i. e., will not reproduce on fluoride-free wort agar. The number of living cells decreases, passes through a mimimum, which may be less than one in 1200 of those originally present, and then increases. Selection plays a part in the acclimatization.

(9) Measurements of the rate of reproduction of yeast in wort with and without ammonium fluoride, show that the cells which are not killed outright undergo a period of paralysis, after which they reproduce, giving rise to fluoride-resistant cells. Adaptation plays a part in the acclimatization.

A maximum value for the duration of paralysis may be calculated from the experimental results.

The University of Toronto, May, 1921

THE OXIDATION AND LUMINESCENCE OF PHOSPHORUS. III*

BY HARRY B. WEISER AND ALLEN GARRISON

The Catalytic Action of Vapors

It has been known for a long time[1] that the vapors of certain substances such as ethylene, ether and turpentine have the power of preventing the oxidation and so extinguishing the luminescence of phosphorus. The first quantitative work was done by Graham who sought the partial pressure of oxygen at which oxidation ceased by diluting air with various vapors until the glow was extinguished. In this way he found that at 25° the glowing of phosphorus was extinguished by: 1 volume of ethylene in 450 volumes of air; 1 volume of ether in 150 volumes of air; and 1 volume of turpentine in 1440 volumes of air. Graham next tried the addition of more of a given substance than was necessary to extinguish the glow; and found that it was necessary either to raise the temperature of the mixture or to lower the partial pressure of the oxygen in order to obtain a reappearance of the luminescence. These early observations were not extended materially[2] until 1898 when Centnerszwer[3] studied the catalytic influence on the luminescence of phosphorus of a large number of gases and vapors, including 19 aliphatic and 11 aromatic compounds. Centnerszwer introduced phosphorus into a mixture of oxygen with a known amount of the vapors of the catalyst. The pressure was reduced slowly with an air-pump and the point was noted at which luminescence first appeared. A large number of determinations was made for each catalyst at different concentrations;

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* The last of a series of articles taken from a thesis presented by Allen Garrison to the Faculty of the Rice Institute in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[1] Berthollet: Jour. de l'école polyt., **3**, 274 (1795–6); Graham: Quart. Jour. Sci., **6**, 83 (1829); Pogg. Ann., **17**, 375 (1829); Davy: Edin. Phil. Jour., **15**, 48 (1833).

[2] See, however, Deschamps: Comptes rendus, **52**, 355 (1861); Vogel: Jour. prakt. Chem., **19**, 394 (1840); Joubert. Thesis, Paris (1874).

[3] Zeit. phys. Chem., **26**, 1 (1898).

and the results were plotted using as ordinates the partial pressure of oxygen at which glowing appeared and as abscissas the percentage content of the catalyst. It was found that the glow pressure, under otherwise constant conditions, varied with the manner in which the pressure was reduced so that the curves were quite irregular in some cases. From the curves Centnerszwer calculated A, the lowering of the luminescence pressure for each percent of the catalyst and B, the curvature of the curve. From these results he deduced the following relations between the constitution of the substances and their catalytic action on the oxidation of phosphorus:

1. The constant A increases in an homologous series with increasing number of carbon atoms. One can get an approximate idea of the extent of this increment when one considers that the vapor pressure of homologous substances at the same temperature decreases with increasing molecular weight. In spite of this the glow pressure remains in approximately the same region in the presence of the saturated vapor of all homologues.

2. Isomers appear to have approximately the same effect.

3. A double bond increases the value of the constant A.

4. The substitution of chlorine or bromine has but a slight effect on the constant.

5. On the other hand, the substitution of iodine increases the catalytic action to a high degree. The iodides are the strongest catalysts of all the substances studied. It requires but a small amount of an iodide to destroy the luminescence entirely, e. g., 2 percent of allyliodide.

6. The action of esters is slight.

7. The variation from a straight line (value of the constant B) is greater, the greater the value of A. The deviation of benzene and its homologues is particularly marked.

Centnerszwer points out that the constants determined are not exact and that the results should serve merely as a starting point for more exact determinations.

Attention should be called to the fact that all the organic substances mentioned by Centnerszwer in his original communication acted as negative catalysts. He found that a small amount of water vapor favors the oxidation of phosphorus[1] and confirmed Chappuis'[2] observation that ozone is particularly active as a positive catalyst. No explanation was offered for the catalytic action in any case. He pointed out that Schönbein[3] is probably incorrect in attributing the negative catalytic action of vapors to their destructive effect on ozone. For example, turpentine is one of the strongest catalysts and yet it is apparently inactive toward ozone.

Russell[4] found that a trace of water catalyzes the oxidation of phosphorus positively but that a maximum is soon reached after which further additions of water vapor have a retarding influence. The presence of more than a trace of water vapor must act as a negative catalyst in the same way as the vapors of the other substances studied by Centnerszwer.

Scharff[5] has investigated qualitatively the effect of various vapors on the luminescence of phosphorus trioxide and finds that, in general, the results agree with Centnerszwer's observations on the action of vapors on the luminescence of phosphorus. As a possible explanation of the phenomenon, Scharff suggests that the organic vapors are adsorbed on the surface of phosphorus or react with the oxidation products as phosphorus trioxide, forming a liquid layer which protects the phosphorus from further evaporation. Scharff's view is opposed by Centnerszwer[6] who carried out a series of experiments to demonstrate that phosphorus vaporizes in various gases even when no luminescence can be detected. A measured volume of various gases was conducted over a weighed amount of phosphorus at a definite temperature and the loss in weight of the phosphorus due to evaporation was determined

[1] Cf. Ewan: Zeit. phys. Chem., **16**, 315 (1893).
[2] Bull. Soc. chim. Paris, **35**, 419 (1881).
[3] Jour. prakt. Chem., **36**, 247, 379 (1845).
[4] Jour. Chem. Soc., **83**, 1263 (1903).
[5] Zeit. phys. Chem., **62**, 179 (1908); Dissertation, Marburg (1907).
[6] Zeit. phys. Chem., **85**, 99 (1913).

by direct weighing. The procedure was as follows: "Small pieces of phosphorus 4 cm in diameter and 6 cm long were placed in a porcelain boat. Three sticks were arranged one after another in a glass tube through which flowed a slow stream of the gas under consideration. Usually only the first piece of phosphorus showed evaporation; the second often showed a loss in weight of a few milligrams; the weight of the third usually remained unchanged. From this one concludes that the saturation of the gas with the vapors of phosphorus is reached."

The first experiments were carried out with moist oxygen obtained electrolytically from the electrolysis of sodium hydroxide. The temperature was approximately 20°. The average amount of gas passed over the phosphorus was 70 litres. A summary of the results is given in Table 1.

TABLE 1

Litres of gas	Loss in weight of three pieces of P, mg			Loss in weight of P per 100 litres of O_2 mg	Vapor pressure of P, mm
56.0	6.2	—	—	11.1	—
98.0	10.6	—	—	11.8	—
45.0	4.4	4.8	—	20.7	0.0303
36.5	3.6	3.6	—	19.7	0.0292
86.5	5.3	1.7	1.8	10.2	0.0150
80.3	8.8	6.6	—0.8	19.2	0.0284
75.0	10.4	2.2	—0.2	16.8	0.0248
75.0	9.2	1.4	1.1	15.6	0.0230

It will be noted that the data in the above table are very irregular—a result that might be expected when we consider the experimental difficulties involved. Nevertheless, the conclusion is reached that phosphorus vaporizes in a stream of pure oxygen and that the phosphorus vapors remain in pure oxygen at atmospheric pressure without undergoing oxidation. In support of this view, Centnerszwer found that a luminous cloud was formed when the oxygen passed over phosphorus was lead into the air. He claimed that this luminescence could not be due to the presence of phosphorus trioxide for the same results were obtained when the gas was allowed to stand

over water for some time—a procedure calculated to remove phosphorous trioxide.[1]

Further experiments were carried out with hydrogen, carbon dioxide and air containing the vapors of iodobenzene. It is probable that oxygen was not entirely absent in any case. From the results Centnerszwer concluded that: "1. Phosphorus vaporizes in pure oxygen and obeys the Dalton law; 2. Gases and vapors which prevent the oxidation of phosphorus are without influence on its evaporation; 3. The catalysts which prevent the oxidation produce no permanent change in the phosphorus."

Centnerszwer states further that: "All these experiments show us quite clearly that the vapors of organic substances do not exert any physical effect on the phosphorus such as condensing on the surface and preventing evaporation. We must rather regard this action as a purely catalytic one without being able to say what physical or chemical process lies at the basis of this catalytic action."

Although most of the substances studied by Centnerszwer act as negative catalysts, he calls attention to the fact that diphenylamine and nitrobenzene are positive catalysts. Chloroform vapors behave peculiarly. At the outset they prevent the luminescence; but after a time the phosphorus "becomes accustomed" to the poisoning influence and begins to glow.

Experimental

The Effect of Catalysts on the Ionization Produced by Oxidizing Phosphorus.—As above pointed out, Centnerszwer and others find that certain vapors have a marked influence on the partial pressure of oxygen at which phosphorus glows. Such vapors have been designated as catalysts. It is known that ions are formed during the oxidation of phosphorus and experiments were carried out to determine the effect on the ions of a vapor that catalyzes the oxidation.

Experiment 1.—The apparatus employed in this investigation was a Wilson tilted electroscope arranged essentially as

[1] Cf., however, Weiser and Garrison: Jour. Phys. Chem., 25, 349 (1921).

shown in Figure 1 of the second article in this series.[1] The only modification necessary was an arrangement to allow a definite mixture of air and catalyst to enter the electrode compartment. The catalyst used was sulphur dioxide since it has a moderately strong inhibiting influence on the oxidation and since it may be used conveniently.

Air and sulphur dioxide were first passed through flowmeters and afterwards mixed. In this way mixtures of a known composition were obtained which were subsequently conducted into the ionization chamber. The total rate of flow of the mixture was held constant but the SO_2 content was varied. As in the experiments without catalyst, the phosphorus was mounted on a movable electrode and the gases

TABLE 2

Distance of phosphorus from electroscope needle, mm	Concentration of sulphur dioxide, percent at 25°	at 27.5
1.0	12.9	38.5
2.0	12.9	38.5
3.0	12.4	37.5
4.0	11.1	35.0
5.0	9.5	27.5
6.0	8.0	20.0
7.0	6.4	9.4
8.0	4.7	—
11.1	0.0	—
12.0	—	0.0

were passed through the ionization chamber at such a rate that the oxidation products were carried away from the space between the electrodes. For a mixture of air and SO_2 it was found that the electric intensity required to draw the ions from the earthed phosphorus was greater than that for air under the same conditions; and that the intensity must increase as the concentration of catalyst increases in order to maintain the same leak from the charged needle. Some quantitative data were obtained as follows: The distance of the phosphorus from the electroscope needle was regulated to the desired

[1] Jour. Phys. Chem., **25**, 349 (1921).

point. The needle was charged to 150 volts and the mixture found at which a leak was just perceptible. A series of experiments was carried out at two different temperatures. The results are given in Table 2.

From the above results it is evident that the conductivity of the air in the region of glowing phosphorus is appreciably decreased by relatively small amounts of sulphur dioxide. As one should expect, a larger concentration of catalyst is required to extinguish the glow the higher the temperature of the mixture. At 25° luminescence ceased in the presence of 12.9% of SO_2 while at 27.5° the glow was not extinguished until the gas mixture was 38.5% SO_2.

Cloud Formation in the Presence of Catalysts.—Since the formation of a dense cloud near the surface of oxidizing phosphorus will tend to slow down the rate of oxidation it was of interest to know whether the vapors which catalyze the reaction will condense on the oxidation products forming a cloud in the same way as water does. This was determined as follows:

Experiment 2.—A solution of phosphorus in ethyl acetate was prepared and dried for several weeks with calcium chloride. This water-free solution was then placed in a small flask closed by a ground glass joint to which a two-way stopcock was sealed. One arm of the stopcock was open to the air; and the other connected with a drying tube containing loosely packed phosphorus pentoxide. With the stopcock open to the first arm, the flask was warmed until all air was expelled and a flame appeared where the combined vapors of solvent and phosphorus met the air. The stopcock was next rotated so that as the flask cooled, air was drawn through the drying tube and thence into the flask. When the flame appeared in the flask a dense cloud appeared even though no moisture was present.

The above experiment was repeated using various catalysts as solvents for phosphorus. Among the solvents used were toluene, methyl bromide, ethyl bromide and iodobenzene. Although particular care was taken to dry the liquids with

calcium chloride or phosphorus pentoxide, a dense cloud formation resulted in every case. From the results, it may be concluded that the phenomenon of water vapor condensation in the region of glowing phosphorus may be extended to the vapors of those substances which are quite active in retarding the oxidation of the element.

The Nature of the Charged Cloud.—It was found that the cloud formed during the oxidation of phosphorus in the presence of vapors contains some substance which will undergo further oxidation with the emission of light. This was shown as follows:

Experiment 3.—Air was drawn through a bubbling bottle containing a colloidal suspension of phosphorus in dilute acetic acid. Oxidation occurred and a dense cloud or fog was formed which was drawn into an outlet tube. The cloud was expanded suddenly by allowing it to pass through a capillary stopcock into a tube 3 cm in diameter and 10 cm in length. By properly adjusting the rate at which the air was drawn and the opening in the stopcock, a flame appeared where the cloud expanded beyond the stopcock and extended throughout the full length of the tube.

Gauze electrodes were sealed in the tube where the secondary luminescence appeared. The charging of these electrodes was without influence on the secondary flame showing that the light was not connected with the recombination of ions or charged particles.

The results of the above experiment show that the cloud formed by the oxidation of phosphorus in the presence of vapors contains particles of some oxidizable material, phosphorus or phosphorus trioxide, which is protected by a film of vapors condensed on the surface. By heating, by sudden expansion or by reducing the pressure, vaporization occurs and oxidation takes place with the accompanying luminescence.

The Absence of Phosphorus Vapor in Oxygen.—The result of the preceding experiment raises the question whether phosphorus or phosphorus trioxide is the oxidizable material which

burns with the emission of the secondary luminescence. It will be recalled that Centnerszwer claims that phosphorus vaporizes in pure oxygen and that this phosphorus vapor will remain unoxidized until the partial pressure of the oxygen is reduced below a certain point—a condition which he realized by allowing bubbles of the gas to escape into the air.

Experiments previously described in detail[1] show conclusively that pure oxygen passed over phosphorus contains no phosphorus but that it does contain phosphorus trioxide which burns with a characteristic flame under suitable conditions. Since the earlier experiments were carried out in the presence of moisture and since a trace of moisture catalyzes the oxidation of both phosphorus and phosphorus trioxide, the experiments were repeated with dry oxygen.

Experiment 4.—A piece of phosphorus was melted in a glass tube 1 cm in diameter and allowed to flow until a fresh surface of approximately 10 cm^2 was obtained. The tube containing the element was surrounded by a water jacket so that the temperature could be regulated. A stream of oxygen dried by passing first through a tower of calcium chloride and thence through a tower of loosely packed phosphorus pentoxide, was conducted slowly over the phosphorus at a temperature so low that the latter did not glow. When the oxygen passed over the element was heated by conducting through a U-tube immersed in water at 70° or above, a cone-shaped flame appeared which disappeared below 65°.

After allowing dry oxygen to pass over the phosphorus until the latter was thoroughly dried, a gas sample-tube was filled with the gases and evacuated slowly in the dark. No luminescence was obtained at room temperature. One end of a tube of the dried gases was next heated slowly. No luminescence was observed until a temperature above 65° was reached at which point an explosion wave or flame filled the tube. The results were entirely different with phosphorus. When a vessel containing phosphorus in contact with pure oxygen was evacuated slowly at room temperature, the element glowed.

[1] Weiser and Garrison: Jour. Phys. Chem., **25**, 379 (1921).

Moreover a glow was obtained when such a system was heated above 27° at atmospheric pressure.

At a temperature between 26° and 27°, the phosphorus in the tube over which a stream of oxygen passed could be made either to glow or not to glow by properly adjusting the oxygen rate. At a very slow rate a flame appeared on the surface of the element but the flame disappeared when the rate of flow of oxygen was increased but slightly. Oxygen which had passed over phosphorus at 26° at such a rate that the element just failed to glow, contained phosphorus trioxide vapors which would not glow until the temperature was raised to 65° to 70°. When this mixture which would not glow under 65° was passed into warm dry air, faint widely distributed flames were seen. The air of the room was usually not sufficiently warm; but the effect may be produced by holding a large warm body such as an iron plate or rod near the point where the gas mixture entered the air. To show that slow oxidation of phosphorus trioxide took place in pure oxygen at ordinary temperature the following experiment was carried out:

Experiment 5.—A gas sample-tube was filled with oxygen saturated with the vapors of phosphorus trioxide. This was allowed to remain at room temperature for 24 hours after which it was heated above 70°. No luminescence was obtained showing that slow oxidation of the trioxide took place at room temperature.

The results of the above experiments merely confirm the previous conclusion that phosphorus trioxide is formed when any gas containing oxygen is passed over phosphorus under such conditions that the element does not glow. This trioxide may be made to oxidize sufficiently rapidly to glow by heating above 65°. The oxidation proceeds slowly at a lower temperature and, when unconfined, the heat of this slow reaction may speed up the process to the critical velocity necessary for luminescence. When confined in a tube, the walls carry away the heat and luminescence is not obtained.

The Effect of Ozone.—Attention should be called to the dif-

ference in the behavior of the oxygen containing phosphorus trioxide and the dense cloud formed by bubbling air through a colloidal solution of phosphorus when the two are subjected to reduced pressure. In the former case no luminescence was obtained at ordinary temperatures while in the latter case the cloud became luminous. This difference in behavior was traced to the effect of ozone present in the cloud.

The oxidation of phosphorus takes place in two steps. L. and E. Bloch[1] have shown that ozone is not formed during the first step, the oxidation to P_4O_6; whereas it is formed during the oxidation of P_4O_6 to P_2O_5. When pure oxygen is passed over phosphorus at room temperature one obtains a very dilute solution of phosphorus trioxide vapors in oxygen. This solution does not give the usual test for ozone. On the other hand the dense cloud formed by bubbling air through colloidal phosphorus gives a marked test for ozone. Schenck[2] states that ozone catalyzes the oxidation of phosphorus trioxide positively. This has been demonstrated in the following experiments:

Experiment 6.—Air was bubbled through colloidal phosphorus and a sample tube filled with the cloud. When the pressure in this tube was reduced a flame appeared as previously described. The tube was again filled with the cloud which was first conducted through a 3-foot length of rubber tubing to destroy ozone. Under these conditions no luminescence was obtained when the pressure in the tube was reduced. The experiment was repeated a number of times with similar results.

Experiment 7.—The cloud obtained by bubbling air through colloidal phosphorus was bubbled through water before reaching the sample tube. Luminescence was obtained under reduced pressure as before, confirming the observation that phosphorus trioxide reacts only very slowly with cold water.[3] A solution of potassium iodide to remove ozone, was substi-

[1] Comptes rendus: **147**, 842 (1908).

[2] Abegg's Handbuch der anorganischen Chemie, **3** III, 421 (1907).

[3] Schenck: Loc. cit.

tuted for the water and the experiment repeated. Under these conditions no luminescence was obtained. If the bubbles were passed through the iodide too rapidly to remove all the ozone, a faint luminescence was obtained under reduced pressure.

The results of the above experiments show the catalytic action of ozone on the oxidation of phosphorus trioxide The dense cloud formed by bubbling air through colloidal phosphorus contained solid particles of pentoxide and trioxide protected by a film of moisture. Reduced pressure favored the removal of the protecting film and vaporization of trioxide, the oxidation of which in the presence of ozone raised the temperature until the critical luminescence velocity was attained. The concentration of trioxide was so low that the rate of oxidation was not sufficiently rapid to produce light in the absence of ozone.

The Action of Nitrobenzene and Diphenylamine.—Centnerszwer found that nitrobenzene and dephenylamine increase the velocity of oxidation of phosphorus just as ozone does. In the light of the experiments with ozone it seemed probable that the positive catalytic action of the two organic compounds resulted from their action on phosphorus trioxide. This view is supported by the following experiment:

Experiment 8.—Some pure redistilled phosphorus trioxide was placed in a test-tube previously filled with hydrogen, and a few drops of nitrobenzene were added. Immediate action was observed which became violent with gentle warming. Similar results were obtained with diphenylamine.

The Effect of a High Potential on the Luminescence of Phosphorus.—When phosphorus is allowed to oxidize in an electric field, the ions formed during the reaction are removed as fast as formed. Since these ions consist of oxide particles about charged nuclei, their removal from the zone of reaction favors oxidation. It was found that the intensity of luminescence is not increased appreciably until a very high potential is obtained probably because the increase in rate of oxidation

is balanced by the removal of phosphorus trioxide particles, the oxidation of which produces the luminescence associated with oxidizing phosphorus.[1] The effect of a very high potential will next be considered.

Experiment 9.—Small lumps of phosphorus of uniform size and shape were prepared; and one was placed on each metal ball of a static machine. The ionization about the phosphorus was sufficient to cause leakage and so prevent sparking until the speed of the machine was increased to such a point that ionization by collision about the phosphorus was large and a brush discharge appeared. At this point, the luminescence on each piece of phosphorus disappeared at the same instant and did not reappear until the potential was lowered to a point where the brush discharge ceased.

Two causes contribute to the disappearance of luminescence at the potential necessary for a brush discharge: first, the removal of charged particles of phosphorus trioxide by the intense field; and second, the sweeping away of vapors of phosphorus trioxide by the very rapid currents of air about the phosphorus surface produced by the discharge—an effect not unlike that of a steady stream of air passing rapidly over the surface.

Discussion of Results

It was pointed out in an earlier communication[2] that if the vapors only of phosphorus are brought in contact with oxygen, and all disturbing elements removed, the velocity of oxidation is proportional to the concentration of the reacting substances. In practice, solid phosphorus is used as a constant source of phosphorus vapor and the products of the oxidation cannot be removed. If the partial pressure of oxygen is so high that oxidation takes place faster than evaporation the action takes place very close to the phosphorus surface where the products of oxidation have a maximum effect both on the rate of evaporation and the available oxygen concentration;

[1] Weiser and Garrison: Jour. Phys. Chem., **25**, 379 (1921).
[2] Weiser and Garrison: Ibid., **25**, 61 (1921).

and where molecular attraction and adsorption are large. Under these conditions the surface will become coated with a film of oxide. Although the thickness of this film may be of molecular dimensions, phosphorus vapor will diffuse through it with difficulty.

It has been shown conclusively that the first step in the oxidation of phosphorus results in the formation of phosphorus trioxide (Experiment 4). Let us consider a piece of phosphorus in dry oxygen at room temperature and at a pressure sufficiently low that the surface of the element glows. Now, when the oxygen pressure is increased, oxidation takes place closer and closer to the solid and disturbing influences which tend to stop oxidation (oxides formed and heat conducted away) become larger. When the reaction has come close enough to the surface for the solid to absorb most of the heat, the reaction slows down. Under these conditions the reaction product is largely phosphorus trioxide since a somewhat higher temperature is required for the rapid oxidation of phosphorus trioxide to phosphorus pentoxide (65° at 1 atmosphere) than for the rapid oxidation of phosphorus to phosphorus trioxide (27° at 1 atmosphere). If a stream of pure oxygen is passed over phosphorus below 27°, oxidation to trioxide takes place and this product may be made to glow by subsequent heating to 65°. Since phosphorus glows in pure oxygen at atmospheric pressure at 27°, it is evident that the heat of formation of phosphorus trioxide under these conditions raises the temperature of the latter to the point where it oxidizes sufficiently rapidly to emit the light that is commonly associated with oxidizing phosphorus.[1]

Since the presence of oxides on or near the surface of phosphorus prevents oxidation, we should expect anything which removes the products of oxidation from the reacting zone to increase the rate of oxidation. Thus it is found that an electric field increases the rate of oxidation by drawing out the ions (oxide particles around charged nuclei), formed during complete oxidation. Conversely, anything that causes the oxide par-

[1] See Weiser and Garrison: Jour. Phys. Chem., 25, 349 (1921).

ticles to cling closer to the surface of the element will decrease the rate of oxidation. The negative catalysts, so-called, act in this way.

We have seen that phosphorus trioxide is the first product of the reaction between phosphorus and oxygen; and this product undergoes oxidation with sufficient rapidity to give light only under suitable conditions. If the temperature is low; if the concentration of oxygen in the reaction zone is low; or if vapors are present which condense on the surface of the particles, the primary product of the oxidation is phosphorus trioxide which can later be caused to oxidize giving a secondary luminescence (Experiment 3). Now it is well known that gases and vapors tend to condense on charged particles forming a charged cloud. Moreover, gases and vapors are adsorbed on uncharged particles particularly if the latter are soluble in the former. If a gas or vapor is adsorbed or condensed on phosphorus trioxide particles and reacts with this trioxide, it will tend to increase the rate of oxidation of phosphorus not only by removing the oxide particles but by raising the temperature. Thus we find that ozone (Experiments 6 and 7), nitrobenzene and diphenylamine (Experiment 8) react energetically with phosphorus trioxide and these substances are designated as positive catalysts by Centnerszwer. If, on the other hand, the vapors are inert toward the oxidation products, their presence will have an inhibiting action. By reason of the charge on the oxide particles, their solubility in various solvents and their adsorbability for various vapors, the latter condense on the oxide particles forming clouds (Experiment 2). A heavy inert cloud formed close to the phosphorus surface tends to slow down the reaction. If two vapors are adsorbed to the same extent, the heavier vapor will form the denser cloud and will have the greater inhibiting action. The presence of vapors which condense on charged particles weight them down and so decrease the conductivity of phosphorized air (Experiment 1).

From the point of view herein outlined, vapors (with the exception of a trace of water vapor) which influence the rate of

oxidation of phosphorus are not catalysts in the ordinary sense in which this term is used. The vapors are merely condensed on the charged or uncharged oxidation products (phosphorus trioxide and pentoxide). If the vapors react with phosphorus trioxide they increase the rate of oxidation. If they are inert, they prevent further oxidation of phosphorus trioxide and also form a cloud near the surface of the phosphorus. The cloud approaches nearer and nearer the surface as the oxidation becomes less and less energetic and in certain cases may form a protecting film that reduces the oxidation to a minimum.

Since the luminescence of phosphorus is due to the oxidation of phosphorus trioxide, we can get oxidation of the element without luminescence if oxygen or gases containing oxygen are passed over it under such conditions that the oxidation is stopped at the P_4O_6 stage. From what has been said, it follows that the film which first forms on phosphorus in pure oxygen below 27° is phosphorus trioxide which is slowly converted to the nonvolatile pentoxide without visible luminescence (Experiment 4). In a stream of pure oxygen below 27° the vaporized phosphorus is converted promptly to trioxide which can be made to oxidize with sufficient intensity to produce luminescence only by raising the temperature. In the absence of a stream of oxygen, any phosphorus vapor which escapes through the film is oxidized so close to the surface that it merely serves to thicken the protection. Since all the gases (except hydrogen) which Centnerszwer[1] conducted over phosphorus contained at least a trace of oxygen and since only a trace of oxygen was necessary to convert all the vaporized phosphorus into trioxide, it is altogether likely that the substance in the gases which would glow under suitable conditions was not phosphorus but phosphorus trioxide.

It is of interest that phosphorus trioxide vapors in oxygen oxidize too slowly to glow when the mixture is confined in a vessel; but that luminescence is obtained when the mixture is allowed to escape into the air of a warm room. Since there is

[1] Zeit. phys. Chem., 85, 99 (1913).

so little trioxide vapor, the concentration of oxygen is comparatively high in either case. Hence, it seems probable, as previously suggested, that the failure of the mixture to react fast enough to glow when confined in a tube is due to the absorption of the heat of reaction by the containing vessel. Until the question has been investigated it is impossible to say whether there is any similarity between the behavior of phosphorus trioxide and phosphine which reacts with pure oxygen at atmospheric pressure but explodes only when the total pressure is diminished.[1]

Summary

The results of this investigation may be summarized briefly as follows:

1. The vapors of a number of organic compounds influence the rate of oxidation of phosphorus. Most of the vapors have been found to retard the oxidation; two of them, nitrobenzene and diphenylamine, accelerate it.

2. Phosphorus trioxide is an intermediate product in the oxidation of phosphorus to phosphorus pentoxide. The rapid oxidation of the intermediate oxide produces light. The temperature necessary for the rapid oxidation of phosphorus to phosphorus trioxide in pure oxygen is less (27° at 1 atmosphere) than for the rapid oxidation of the trioxide to pentoxide (65° at 1 atmosphere). As a rule the heat of the first step raises the temperature in the reaction zone to the point where the trioxide oxidizes with sufficient velocity to emit light. In a stream of oxygen below 27°, the small amount of phosphorus which vaporizes is oxidized to phosphorus trioxide. The latter is converted slowly into pentoxide without the emission of light. In a stream of gas or vapor containing oxygen the chief oxidation product is phosphorus trioxide if the temperature is low; if the concentration of oxygen in the reaction zone is low; or if vapors condense on the surface of the trioxide particles.

[1] Labillardière: Ann. Chim. Phys., **6**, 304 (1817); van der Stadt: Zeit. phys. Chem., **12**, 322 (1893).

3. The ions formed during the oxidation of phosphorus consist of oxide particles about charged nuclei. Vapors are adsorbed or condensed both on the charged and uncharged particles. Condensed vapors decrease the conductivity of phosphorized air by weighting down the charged particles.

4. If the adsorbed vapors react with phosphorus trioxide they increase the velocity of oxidation of phosphorus both by removing oxide particles from the zone of reaction and by raising the temperature. Nitrobenzene and diphenylamine act in this way.

5. If the absorbed vapors are inert they prevent further oxidation of phosphorus trioxide and also form a cloud near the surface of the phosphorus which slows down the action. If two vapors are adsorbed to the same extent, the heavier one will form the denser cloud and will have the greater inhibiting action.

6. It is concluded that vapors (with the exception of a trace of water vapor) which influence the rate of oxidation of phosphorus are not catalysts in the ordinary sense in which this term is used. The vapors are merely condensed on the charged or uncharged oxidation products (phosphorus trioxide and pentoxide). If the vapors react with phosphorus trioxide they increase the rate of oxidation; if they are inert they prevent further oxidation of phosphorus trioxide and also form a cloud near the surface of the phosphorus. This cloud approaches nearer and nearer the surface as the oxidation becomes less and less energetic and may form a protecting film which reduces vaporization and oxidation of phosphorus to a minimum.

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THE FREEZING POINT CURVE OF THE SYSTEM: ORTHO-CRESOL: NAPHTHALENE[1]

F. H. RHODES AND F. E. HANCE

Some time ago there was completed some preliminary experimental work on the approximate freezing points of mixtures of ortho-cresol and naphthalene. In this previous work, which was done under the direction of one of us at the H. W. Jayne Laboratory of the Barrett Company, it was found that ortho-cresol and naphthalene form a eutectic mixture which melts at approximately 20° C, and which contains about 22 percent of naphthalene. Moreover, it was observed that mixtures containing relatively large amounts of ortho-cresol are very easily supercooled; and that in some cases the supercooling can be carried so far that crystals of naphthalene may be caused to separate from mixtures containing very considerably more than the eutectic amount of ortho-cresol. Thus, many such mixtures apparently possess two freezing points—one freezing point corresponding to the temperature at which solid ortho-cresol is in stable equilibrium with mother liquor, and the second and lower freezing point corresponding to the temperature at which solid naphthalene is in metastable equilibrium with a supercooled cresol-rich mother liquor.

Since the study of the freezing points of mixtures of ortho-cresol and naphthalene affords a very good experimental demonstration of the fact that the freezing point curve of a system of this type consists simply of two intersecting solubility curves, it was thought advisable to make a more careful investigation of the freezing point curve for the system ortho-cresol: naphthalene. The results of this work are described in this present article.

The materials used in this work were prepared from refined naphthalene and technically pure ortho-cresol, both of

[1] Contribution from the Department of Chemistry of Cornell University.

which were donated by the Chemical Department of the Barrett Company.

The ortho-cresol was further purified by dissolving it in an excess of a solution of caustic soda, steam-distilling the carbolate solution to remove traces of pyridine and hydrocarbons, liberating the cresol again by acidifying the solution with sulphuric acid, and finally purifying the ortho-cresol by repeated fractional distillation through an efficient fractionating column. The final purified ortho-cresol had a melting point of 30.4° C.

The naphthalene was further purified by dissolving it in pure benzene and shaking the solution with successive portions of concentrated sulphuric acid, water, sodium hydroxide solution, and water, respectively. After distilling off the solvent the naphthalene was distilled. The resulting product was recrystallized from benzene and redistilled through a fractionating column. The final purified naphthalene had a melting point of 80.2° C.

The apparatus used in determining the freezing points of the various mixtures consisted essentially of a large test tube (7″ x 3/4″) provided with a tightly fitting cork stopper through which were inserted the thermometer and the stirrer. This tube was surrounded by a larger glass tube, which was immersed in the cold water used as a cooling medium. The thermometer used in this work was a standardized "Tycos" thermometer, graduated from 0° C to 100° C in 1/10° C.

In making a determination accurately weighed amounts of naphthalene and ortho-cresol were placed in the tube, and the mixture was then melted and then cooled slowly and with constant and regular stirring. As the freezing point of the mixture was approached, the charge was "seeded" by adding small crystals of naphthalene or of ortho-cresol. In each case the temperature taken as the freezing point of the mixture was the temperature at which permanent crystals first appeared.

The results obtained in these determinations are given in the following table:

% Cresol	% Naphthalene	Freezing Point	
		Stable	Metastable
100	0.0	30.4	——
99.5	0.5	30.2	——
99	1	29.9	——
98	2	29.4	——
97	3	29.0	——
96	4	28.45	——
95	5	28.2	——
90	10	25.9	——
85	15	23.6	5.0
80	20	21.9	15.94
79	21	21.2	17.54
78	22	20.8	19.1
77	23	21.3	——
76.5	23.5	21.8	——
75	25	24.3	——
70	30	32.3	——
60	40	43.3	——
50	50	50.1	——
25	75	65.65	——
10	90	74.56	——
0	100	80.2	——

These results are shown by the accompanying graph. One branch, AC, of the curve represents the (stable) equilibria be-

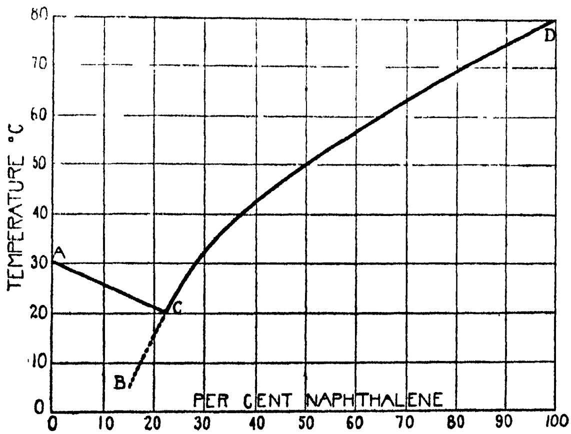

Fig. 1

tween solid and ortho-cresol and solution, while the other branch, CD, represents the equilibria between solid naphtha-

lene and solution. The eutectic, C, contains 22.5% naphthalene and melts at 20.6° C. Line CB represents the continuation of branch DC beyond the eutectic point—i. e., the metastable equilibrium between solid naphthalene and supercooled cresol-rich solutions.

Because of the extent to which supercooling occurs in the cresol-rich mixtures, and because of the ease with which points on the metastable curve CB can be determined, the study of the freezing point curve of the system ortho-cresol: naphthalene affords an excellent experimental illustration of the fact that the freezing point curve of a system of this type is composed of the two intersecting mutual solubility curves.

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THE STRUCTURE OF METAL ELECTRO-DEPOSITED UPON ROTATING CATHODES

BY W. E. HUGHES, B.A.

In a report recently submitted to the Department of Scientific and Industrial Research the author makes some general statements in regard to the crystalline structure of electrodeposited iron. These statements are based on observations made during the examination under the microscope of three series of deposits formed in the ferrous calcium chloride bath.[1] The first series was directed to determine the effect of the temperature of the solution upon the crystalline structure of the deposit; the second sought to ascertain the effect of current density; and the third was concerned with the change (if any) brought about in the structure of the deposit by motion of cathode or solution. The statements made are:— (1) That "the results of both macroscopic and microscopic investigations show that, cet. par., increase of temperature causes increased coarseness of deposit;" (2) that, as regards the effect of current density, "the size of grain appears to alternate; as the current density increases, the size of grain at first increases also, then diminishes, and then seems to increase again;" and (3) "the effect of movement of the cathode upon the structure of the deposits is . . . . . that movement causes diminution of grain size: microscopic examination confirms visual observation." Explanations of these effects are attempted: they are, each and all, founded upon the proposition that the crystalline structure of deposited metal is determined, at bottom, by one thing, namely, the concentration of free and available[2] metal atoms in the immediate cathode neighborhood—that other factors count only in so far as they contribute to or detract from that concentration.

[1] Sometimes known as the Fischer-Langbein solution.

[2] It is necessary to make this reservation in order to meet such cases as those of sodium, magnesium and others, where chemical action occurs between discharged atom and the electrolyte, and hence the metal atom is not available for deposit formation.

The above statements and the general proposition upon which the explanations are based are reproduced here for the sake of convenience in discussing the cause of the structure of metal deposited upon a rotating cathode. It is necessary, in addition, to remark at once, that the presence of free acid in the electrolyte sometimes causes a profound modification in the structure of deposited metal. This has been noticed by A. Sieverts and W. Wippelmann for the case of copper,[1] and by the present author for iron deposited from the chloride bath.[2] Others have noted the occurrence of modifications in the case of other metals.[3] The modification, as observed macroscopically, consists in a diminution of the size of grain of which the deposit can be seen with the unaided eye to consist. The change of structure, as viewed through the microscope, is seen to consist in a change from V-shaped grains to those having the shape of threads or fibres. The author has called these two types of structure of deposited metal "normal" and "fibrous," respectively. It is unknown how this change is brought about and the proximate cause of the change will not be considered here. One remark only will be made—that the effect of acid in modifying the structure of deposited metal is much more pronounced in the cases of some metals than in those of others: it is much more pronounced in the cases of iron, nickel, or zinc than in those of copper, antimony, or tin.[4] With that remark the effect of acid will cease to be considered but it is to be understood that what is said upon the factor suggested as the determining one, namely, concentration of free and available metal atoms, is subject always to the condition that the modifying effect of free acid (of hydrogen ions, that is) does not come into play.

It is well nigh a common place, now-a-days, to repeat that electro-deposited metal is a crystalline substance: no

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[1] Zeit. anorg. Chem., **91**, 1 (1915).

[2] Trans. Faraday Soc., 1921.

[3] Cf. W. D. Bancroft: Trans. Am. Electrochem. Soc., **21**, 233 (1921).

[4] Cf. Sieverts and Wippelmann: Loc. cit., and W. Pfanhauser: "Die elektrolytischen Metallniederschläge," p. 675.

instance of solid, non-crystalline electro-deposited metal has, so far as the author is aware, ever been illustrated and described in a serious scientific publication. Some loose statements—obiter dicta, for the most part—have been made to the effect that, in this case or that, the deposited metal is "structureless" or "amorphous;" but it does not appear that in any of these cases the matter was scientifically investigated. Hence, statements of this kind may be dismissed with the following few remarks. As regards one class of deposits cited, namely, those formed in cyanide solutions, concerning which it has not infrequently been said that they are structureless, the author can very definitely say, of his own knowledge and as the outcome of his own observations, that such deposits are most certainly *not* structureless.[1] They cannot be seen to have a structure, if the unaided vision is used, nor, sometimes indeed, when the eye is aided by low power magnification only; but if sufficient resolution is obtained (as it can be) by the use of an objective of suitable aperture and a suitable medium, then the structure appears plain enough. This applies, in the author's experience, to a deposit of but five minutes' duration, formed in a solution of copper cyanide of the usual composition.[2]

Electro-deposited metal being then crystalline matter, the laws governing the crystallization of other substances, for example, salts and rock magmas, may be expected, as F. Foerster points out,[3] to apply to such metal also. This has been recognized by other authors—by, *inter alios*, H. Freundlich and Fischer,[4] R. Marc,[5] V. Kohlschütter,[6] W. D. Bancroft,[7] A. H.

[1] A similar remark applies to deposits formed in solutions containing colloidal substances. The author has photographic proof that such deposits are not structureless—at least in the cases of the large number of examples examined by him.

[2] Copper carbonate, potassium bi-sulphite and bi-carbonate of soda.

[3] Elektrochemie wässeriger Lösungen, 328 (1915).

[4] Zeit. Elektrochemie, **18**, 886 (1912).

[5] Ibid., **19**, 431 (1913).

[6] Helv. Chim. Acta., **3**, 614 (1920); **4**, 45 (1921).

[7] Loc. cit.

W. Aten and L. M. Boerlage,[1] to mention a few only. It is, therefore, to be anticipated that the factors which determine the size and shape of grain of such other crystalline substances may operate with similar effect in the case of deposited metal. These factors are solubility, latent heat of precipitation, concentration, viscosity, the dielectric of the solvent, and several more. But von Weimarn has taken solubility and concentration as the most important for consideration,[2] even in the case of salts: *a fortiori*, in the case of deposited metal, many, or even most, of them will, from the very nature of things, be of much less influence and effect in determining grain size. It is difficult to understand how such factors as latent heat, or molecular weights of solvent or precipitate, can operate to any material degree; and the solubility of the deposited metal cannot easily be conceived to play an important rôle, except in so far as solubility affects the concentration of free and available metal atoms in the cathode layer of electrolyte. As has been already pointed out, the temperature of the electrolyte, current density, and the movement do, each of them, play an important part, but this is on account of their effects upon concentration. Aten and Boerlage have[3] lately suggested that the tension of polarization has an important effect upon the crystallization of electro-deposited metal. The author is disinclined to, at present, accept this view for reasons which will be set out elsewhere. Whether metals[4] or rock magmas,[5] solidifying from the molten state, or salts, crystallizing from solutions,[6] are considered, the dominant factor determining grain size is undoubtedly concentration; and the author has pointed out the dominance of this factor—concentration—in the case of electro-deposited metal.[7] It is

[1] Rec. Trav. chim. Pays-Bas, 39, 720 (1920).

[2] "Grundzüge der Dispersoidchemie," 39 (1911).

[3] Loc. cit.

[4] J. A. Ewing: "The Molecular Structure of Metals," Phil. Mag., 12, 256 (1906). See also A. Sauveur: The Metallography of Iron & Steel," 88 (1916).

[5] J. P. Iddings: "Igneous Rocks," 1, 190.

[6] W. D. Bancroft: Jour. Phys. Chem., 24, 105 (1920).

[7] Namely in the report already referred to.

suggested that it is from this point of view that the structure of metal electro-deposited on rotating cathodes must be considered; and it is hoped to justify the suggestion in what follows. That is the object of this paper.

The matter first arose for the author's consideration some few years ago, in connection with the installation of a plant for depositing copper on iron cylinders, and their use, when copper-plated, in the printing trade. When the literature was consulted, it was found that two authors, namely, S. Cowper Coles[1] and J. G. Zimmerman,[2] had within recent years published work on the subject of depositing copper on rotating cathodes, the former in connection with printing rollers, the latter using small pieces of solid metal, cylindrical in shape. Cowper Coles' work was technical; Zimmerman's was scientific. The work of these investigators was not the first to be done on the electro-deposition of metals on rotating cathodes (cylinders or mandrils). That of Henry Wilde is well known, and perhaps still better known, at any rate in commercial circles, is the work of F. and A. S. Elmore. But Wilde does not appear to have concerned himself at all with the structure of the deposited metal: the Elmores did; but the operation of an agate burnisher upon the surface of the copper during deposition naturally introduced a condition that, in all likelihood, prevented the free development of the grains of the deposit that always occurs under conditions of deposition where external mechanical forces are absent.

Both Cowper Coles and Zimmerman concluded, as one result of their experimental work, that the macroscopic aspect of a copper deposit, formed upon a rotating cathode, is determined by the "critical speed" or "critical current density," as they, respectively, say. "The fineness of grain," says Zimmerman,[1] "is dependent upon the current density, other things being equal, and the fineness increases with the current density until, at a critical value, a powdery deposit will occur.

[1] Trans. Faraday Soc., 1, 215 (1905).
[2] Trans. Am. Electrochem. Soc., 3, 245 (1903).

The increase in the number of revolutions per minute increases the critical current density."[1] This is an experimental fact, and one that is not confined to *rotating* cathodes. It is a well-known fact, that, in the ordinary process of electroplating, a higher current density can be employed where the cathode or solution is moved (mere to and fro movement of the cathode rod is sufficient) than can be used where, all other conditions remaining the same, there is no mechanical movement. It was, however, contended in the discussions on Cowper Coles' and Zimmerman's papers that the highly "polished" surface soften, but by no means always, possessed by the copper deposited on rotating cathodes is due to a "decided frictional action" of the liquid (electrolyte) on the copper,[2] or, in other words, to the "burnishing effect of the skin friction."[3] This suggestion was made by Zimmerman himself, when considering the case of zinc. He says (op. cit., p. 249):—"While copper and nickel can be deposited in a high state of polish, zinc cannot be obtained smooth unless special precautions are employed. The smoothest deposit was obtained *by increasing the friction of the solution against the metal,* through the aid of a partition in the cell which prevented the electrolyte from taking up a circulatory motion to correspond with the cathode." The alternative suggestion made in the discussions was that the rotation effected the renewal of metal ions in the layer of electrolyte next the cathode surface. This is the suggestion that the present author supports as the chief cause of the "polished" surfaces obtained on rotating cathodes. At the same time, as before indicated (p. 496) the acid content of the electrolyte—at any rate in the cases of the copper solutions used by both Cowper Coles and Zimmerman—may be a contributory cause. Apart from any effect of free acid, the contention of the author is, that the "polished" appearance of metal electro-deposited upon rotating cathodes is due to the maintenance of the concentration of metal ions at the cathode

[1] Op. cit., p. 246.
[2] Cf. C. F. Burgess: Discussion on Zimmerman's paper, p. 250.
[3] W. C. Prebble: Discussion on Cowper Coles' paper, p. 234.

surface—that it is this maintenance of great concentration of metal ions at the cathode surface which enables the deposit to possess such a structure as to make it appear to the unaided eye smooth and "polished." There are several considerations that negative the "skin friction" view, just as there are other bases to support the alternative one: but the author's support of the latter is founded upon his study of electro-deposited metal under the microscope, and it is the convincing observations made in the course of that study which it is wished to adduce here.

1. It has been shown[1] that if two deposits be formed under exactly the same conditions of deposition, except that, in the one case, the cathode is moved, while, in the other, it is stationary, the deposit in the former case will appear to the eye smooth and structureless, and in the latter it will look crystalline—brilliant and sparkling. It is shown by means of micrographs, that the deposit on the stationary cathode is composed of V-shaped grains, while that on the moved cathode consists of very narrow fibres. Further, it has been shown[2] that the effect of stopping the cathode movement is to produce a change in structure from "fibrous" to "normal" (i. e., one composed of V-shaped grains). The movement used in these cases was merely a to and fro motion of the rod from which the cathodes were suspended, but it was sufficient to effect the changes in structure described. There could be no question here of "polish," burnish, skin friction, or the like.

2. It has also been shown[3] that where a deposit (of iron) has been formed upon a small cylindrical cathode, similar to those used by Zimmerman, and a section cut parallel to the base, polished, and etched, the structure of the deposit may vary round the annulus. This is explicable as due to the cathode not being suspended vertically in the electrolyte, and the play of concentration currents.[4] These currents can be

[1] In the report referred to.

[2] Beama Journal, May, 1921 (fig. 2, facing p. 424).

[3] In the report referred to; also Jour. Iron & Steel Inst., **101**, 336, and plates IX and X (1920).

[4] Cf. H. Sand: Zeit. Elektrochemie, **10**, 452 (1904).

easily seen in operation, if one watches, through the walls of a glass containing-cell, a cathode that is being deposited upon: the liquid round the cathode is seen to rise in streams. The cause of the currents is the same in the case of metal deposition as in that of crystallization of salts from solutions.[1] The liquid round the cathode from which metal has been removed by electrolysis becomes lighter thereby, and, consequently, rises: metal-laden solution falls to take its place. There exist, therefore, in the solution streams or currents due to differences of density that are analogous to convection currents due to differences of temperature. If, then, differences of structure are produced by differences of concentration, one may expect the concentration currents to occasion structural differences; and one can expect, on the concentration hypothesis, that where the currents operate to reduce the concentration of metal the structure will be more visibly crystalline than in places where the concentration is maintained greater and more uniform. These expectations are realized in the case of a cylindrical cathode suspended aslant in the plating solutions. The current density being greatest at the bottom end of the cathode the liquid there is soonest deprived of its metal. This, becoming lighter, rises: it rises up along the cathode surface, and dilutes the solution on the upper parts of that surface, and heavy, metal-laden solution takes its place. As a fact, often observed by the author, the upper surface of the (cylindrical) cathode is usually more or less visibly crystalline in cases where the lower (underneath) surface is matt (or, even, bright) and apparently structureless. One would expect, therefore, to find, on examining with the microscope a section cut parallel to the flat end of the cylinder, that the structure of the annulus varies in size and shape of grain from below upwards. And one finds in fact what one expects to observe. The structure of the lower portions is, nearly always, smaller than that of the upper parts. Sometimes, as, for instance, in the case of the deposit shown in the paper to which reference

[1] Cf. H. A. Miers: Proc. Roy. Soc., 79, 322 (1907).

has been already made, the structural difference is very marked: the structure of the underneath part may be fibrous, while that of the upper part is "normal"—consists, that is to say, of V-shaped grains. There can and do, therefore, exist macroscopic differences of aspect at different parts of the surface of one and the same deposit: these differences may be so great that at one part the deposit appears bright (even "polished") and structureless, while at another it is obviously crystalline. These macroscopic differences correspond to microscopic ones: the bright or matt and apparently structureless deposit is seen, under the microscope, to be of small grain—it may be, and often is, fibrous, while the visibly crystalline deposit consists of larger grains, having more or less the shape of the letter V. These differences can be accounted for on the concentration hypothesis: skin friction, polishing, or burnishing cannot possibly operate to produce them.

3. In the foregoing, numbers 1 and 2, the cathodes were not rotated during deposition. In the one case it was moved to and fro simply, while in the other, neither it nor the solution was moved by external mechanical means. Nevertheless, consideration of the deposits formed upon them is germane to the present discussion, which is intended to show that concentration of available metal atoms is a sufficient cause for the high "polish" often obtained on the deposits formed upon rotating cathodes, and that the means whereby such concentration may be effected is either by agitation of the electrolyte or movement of the cathodes by external mechanical means, or by the operation of such physical agents as concentration currents. The case of the rotating cathode will now be considered.

In the preliminary work done in connection with the deposition of copper on printing rollers, it was found that the current density employable depended (as stated by Cowper Coles and Zimmerman) upon the speed of rotation of the cylinder. Speed of rotation (revolutions per minute, simply) was not however, in and by itself, determinant. The weight and radius of the cylinder were important factors: in other

words, the angular momentum and peripheral speed[1] played an important part. Furthermore, any "whip" of the lower (free) end interfered in that this caused a vortex or whirlpool to be formed around the cylinder, and there could easily result the formation of an air space between the solution and the face of the cylinder—an air space which had place over a greater or less length of it. To avoid this, blades, fixed parallel to the cylinder's axis and at an angle to a tangent at the surface, were used, in accordance with a suggestion made by Zimmerman. The blades met the catholyte rotating in the same direction as the cylinder, and threw it back on to its surface. These facts led the author to think at first that friction might have something to do with the "polished" surfaces that could be obtained under certain conditions in particular cases, the conditions varying from cathode to cathode and including the conditions of deposition proper, such as current density, acidity, and concentration of copper sulphate. But examination of the microstructure led to the contrary belief, namely, that friction had nothing at all to do with the matter. It was found by observation: (1) that the coarser the grain of a deposit appeared to be when examined with the naked eye, the larger the grains appeared to be under the microscope. The structure varied between columnar and "normal," the grains in this latter case being V-shaped, but having very acute angles on the cathode side of the deposit; (2) that, as the visual coarseness of grain diminished the columnar structure became more marked and the grains narrower; and (3) that the structure of the highly "polished" deposit was completely fibrous—it consisted of very narrow or thread-like grains of metal. Moreover, it was found—(4) that there was no indication at all of any burnishing action having taken place. The direction of the grains was approximately perpendicular to the cathode surface, and grains varying from perpendicular were directed, quite impartially, either in the direction of rotation or against it. In connection

[1] Cf. Cowper Coles: Loc. cit.

with number (4) it is right to refer to some remarks of R. Amberg. Concerning deposits formed upon rotating cathodes, Amberg says:[1] "If the liquid rotates very fast, then there is another point that deserves attention: the pressure, which it exercises on the walls of the vessel, is here exercised on the cathode. If one bethinks that, in works practice, a denser kind (*Beschaffenheit*) of, for instance, electrolytic copper is produced by the direct, albeit light, pressure of solid bodies,[2] it is easy to understand that the discharged metal also can acquire a more solid texture as a result of the pressure caused by the rotation. In fact, it is observable how even small particles, separated as sponge, adhere with great tightness to the cathode, and that a thin layer of sponge allows itself to be covered with compact metal. The mode of action of this pressure is comprehensible, if one supposes that it, at the moment of discharge of the metal ions (which one has to look upon as a rapid but continuous passage from liquid ionic to the discharged solid (so-called) state, by way of the colloidal condition), hastens the gel formation, just as shaking, knocking, and so on, destroys colloidal solutions; an analogous case is that of the marked emballing of silver chloride under the influence of vigorous rotation." With regard to Amberg's remarks, which are based on assumptions and analogy and not, for the most part, on experimental facts, it may be said that nothing in the structure of copper deposited upon rotating cathodes points to the operation of such forces as he mentions to produce the kind of surface under consideration. On the contrary, the structure shows nothing other than what one expects as the result of the crystallization process.

Discussion

In none of the foregoing instances, numbers 1, 2, and 3, does anything appear in the structures of the deposits that cannot be explained by the concentration hypothesis. The differences of structure that occur are differences of grain form

[1] Zeit. Elektrochemie, 10, 855 (1904).

[2] Presumably, something in the nature of "buffing" is here referred to.

and grain size, and it is suggested that differences of concentration account well for these structural differences of form and size. In number 1, it is seen that mere to and fro movement of the cathode is sufficient to produce a fibrous structure, and that, if the movement cease for a while, the structure changes to "normal," becoming fibrous again when the motion recommences. It is, therefore, motion that effects the the change. The motion is, in this case, slight; yet it is sufficient to produce the fibrous structure—an internal structure which corresponds to a smooth and matt or bright surface. These are experimental facts. There does not appear to the author to be any other way of accounting for these facts than that of supposing the motion to maintain constant the concentration of metal ions at the cathode surface. If this view is correct, then the fibrous structure is the result of the upkeep of the concentration, and consequently, the concomitant smoothness and the, apparently, structureless aspect of the cathode surface are results of concentration too. Considering the second case, one notes that where, through the play of concentration currents, the metal concentration is maintained uniform, there the deposit has a smooth and, apparently, structureless surface and a fibrous internal structure. But, on the contrary, where the concentration is diminished, through the same agency, there the surface is crystalline and the interior is "normal" in structure. In this case the movement is such that it is scarcely conceivable that friction can be an operative cause in the production of the external and internal characteristics of the deposit. As indicating the contrary, it is to be noted that the smoothness of the deposit's surface is greatest just where the friction is least and the metal concentration greatest, namely, at the lower end and underneath parts of the cathode. The effect of concentration currents can be, as experiment shows, either to cause a crystalline surface and "normal" internal structure, or to produce an, apparently, structureless external surface and fibrous interior. Concentration currents differ, therefore, from mechanical movement, which always produces a structure of smaller grain—

one which is fibrous, and one which is fibrous everywhere and not merely locally, and this even where the movement is so slight as in the case of the to and fro movement of the cathode in case 2. The immediate effect of mechanical movement is, then, to destroy that action of concentration currents which would result in diminishing the metal content of the solution at some parts of the cathode surface. Mechanical movement is, therefore, a more effective agent than concentration currents producing a smooth surface and fibrous structure; the former is not merely local in effect, the latter is. Thirdly, as regards number 3, rotation of the cathode is one kind of mechanical movement. The rotation can be slow or rapid. Experiment shows that speed of rotation and current density are inter-dependent for one and the same cathode, metal concentration of electrolyte, and so on. The greater the speed of rotation is, the higher the current density can be. Experiment shows also that current density and metal concentration are inter-dependent. It is on this inter-dependence that the composition of modern nickel-plating solutions is based, consciously or unconsciously. The greater the metal content is, the higher, *cet. par.*, the current density can be. In the case of rotating cathodes also, therefore, there are three interconnected factors to consider, namely, speed of rotation, current density, and metal concentration; but, of these, metal concentration is of much greater importance in the case of rotating cathodes than in other cases, that is to say, where slow movement occurs (as in number 1) or where concentration currents, diffusion, and the like operate (as in number 2). With rotating cathodes, much higher current densities are usually employed than in other cases.[1] Whereas with rotating cathodes a current density of 100 to 200 amperes per square foot is frequently used, it seldom exceeds 20 amperes per square foot in cases of "still vat" work or where slow mechanical movement of cathode or solution is employed. It is

[1] The Fischer-Langbein process for iron deposition is an exception; but here the metal concentration is very high. See D. R. P. No. 212994 (1908).

convenient for purposes of discussing the deposits on rotating cathodes to rule out the metal concentration factor, which, in and per se, can support the concentration hypothesis only; and this can be done by assuming that, in each case, the deposition of metal proceeds to the extent required by Faraday's law—whatever the current density employed. It is then necessary to consider the inter-connection of speed of rotation and current density only, and the effect of this upon the internal structure and external surface of the deposited metal. Experiment shows that these two factors can be so variously adjusted that one can obtain a surface that varies in appearance from dull and matt to "polished." Microscopic examinations show that as the surface varies from dull and matt to "polished," so the grain size of the metal continuously diminishes. It is certain, on the assumption made as to the requirements of Faraday's law being fulfilled, that, as the current density increases, more metal is discharged at the cathode; hence, so far as this factor operates to produce the diminution of grain size, it must do so by way of concentration. It has been shown, in case number 1, that the fibrous structure and smooth surface is obtained by movement where without it a "normal" interior and crystalline surface would be obtained, and that this is so, although no burnishing or its equivalent could take place, and, therefore, replacement of metal ions must be the operative cause—apart from current density. It therefore seems to the author to be a fair—and, indeed, the only—deduction that rotation, which is only a mode of mechanical movement, operates in the same way as, but more powerfully than, the to and fro movement, and, by effecting a more rapid replacement of metal ions at the cathode surface, enables a greater current density to be employed. The result of both kinds of movement is the same, namely, diminution of grain size within and smooth and, in the optimum case, "polished" surface without. There is, in the result, a difference of degree, but no difference of kind. On the other hand, it is to be noted that, for a given speed of rotation and a given cathode, the "polished" appearance occurs at a certain maximum cur-

rent density, which depends upon the particular speed employed. Below that maximum, the deposit appears matt, and not "polished." Hence, where most metal is being deposited, friction would have its greatest burnishing effect, if this was the cause of the "polish." This is contrary to all likelihood; and the very improbability of such occurrence supports the view that rotation is effective through replacement of metal, for this is the only alternative.

Summary

It is suggested—(1) that the "polished" appearance often observed of the surfaces of deposits formed upon rotating cathodes is due to the smallness of the grains of which the deposits consist; (2) that that smallness of grain is the result of the constancy of metal concentration at the cathode surface; and (3) that, since mechanical movement can maintain constant the metal concentration, rotation of the cathode, which is a mode of mechanical movement, operates in that way in the cases of deposits formed upon rotating cathodes, and not by way of burnishing or the like, as suggested by some other authors.

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NEW BOOKS

Thermodynamics and Chemistry. *By F. H. MacDougall. 22 × 15 cm; pp. v + 391. New York: John Wiley and Sons, 1921. Price: $5.50.*—In the preface the author says: "No one can write on thermodynamics without being deeply influenced by Willard Gibbs and Max Planck. The writings of the former will always be the admiration (and sometimes the despair) of the student of thermodynamics on account of the extreme rigor and completeness with which he discusses the subject, while Planck in his Lectures on Thermodynamics has given a treatment which is a model of conciseness, accuracy and logic. It has been my endeavor to write a book which, in addition to being accurate, logical and sufficiently rigorous, will furnish the student with numerous examples of the application of the principles of the science. It is with this object in view that four chapters have been devoted to the phase rule and its applications."

"This book has been written to meet the needs of advanced students of Chemistry. While a course in thermodynamics is indispensable to students of physical chemistry it is no less desirable for the organic chemist, who finds that, to an ever increasing degree, he must make use of physico-chemical methods and laws, the full significance of which will hardly be clear to one who is not familiar with their thermodynamic foundations. Moreover, the instructor in general of analytical chemistry, if he is not already acquainted with the principles of thermodynamics, will find that a knowledge of them will be of great service to him, both in the class-room and in the laboratory. Many of the laws which we meet with in text-books of Chemistry are valid only under certain definite conditions. Chemical literature is full of instances in which writers have employed these laws in cases in which they are no longer valid. An exact knowledge of the conditions under which these laws may be applied would have prevented this waste of time and energy."

The subject is presented under the following heads: temperature; actual gases; heat; the first law of thermodynamics; applications of the first laws; thermochemistry; the second law of thermodynamics; deductions from the first and second laws; thermodynamic functions and thermodynamic equilibrium; fusion; evaporation, and sublimation; the phase rule; applications of the phase rule; chemical equilibrium; chemical equilibrium in liquid solutions; electromotive force; surface tension and adsorption; radiation, quantum theory, Nernst heat theorem.

This is a perfectly good book and the author has done what he tried to do, except that he has left out Storch's formula on p. 296 and that he states on p. 344 that we only measure adsorption because we cannot measure the surface tension of solids. The point that interests the teacher of chemistry is not whether this or any similar book is good of its kind; but whether it is the kind of book that is good for the student. On this great question the reviewer admits that he is an extremist and that his opinion is not that of the majority. The modern thermodynamical chemist appears to be a purely formal creature who writes pages of formulas instead of putting the subject clearly in relatively few words. To men like the author thermodynamics is an end in itself. To the reviewer thermo-

dynamics should be an instrument of research. We have had a good many years of thermodynamical chemistry in America and it seems to the reviewer that the results obtained in the last quarter-century are pitifully scanty although the gross output is enormous. Old results have been rewritten and new terms have been coined; but that is not what the reviewer wants.

We do not know anything quantitative about the relation between the heat of dilution and apparent osmotic pressure at constant temperature. In our so-called rigorous thermodynamical relations for the distribution law, we ignore the changing miscibility of the two solvents. We write equations for the chemical potentials; but we do not deduce a theoretical formula for the dineric equilibrium between benzene, alcohol, and water to take the simplest experimental case. We use Henry's law for one component and the relation is specific. We use the van't Hoff-Raoult formula for the other component and the relation is general. The thermodynamical formulas for the partial pressures of mixtures of two liquids contain no term for the molecular weights in the liquid phase. We treat a dissolved substance exclusively as a gas even though we know that in most respects it behaves like a liquid. That precludes any adequate discussion of the Soret phenomenon. We do not discuss the question whether there is a real difference between solvent and solute because we put in the definition that the solute is the substance which does not pass through the semipermeable membrane which is not there. When this fails us, as in three-component systems, we speak qualitatively of thermodynamic environment and let it go at that.

We know that the Gibbs formula for the lowering of surface tension applies only to true solutions and we proceed to apply it to colloidal solutions. We find experimentally that certain colloidal solutions do show marked surface concentrations; but we turn in vain to the mathematical chemist for a quantitative or a qualitative explanation.

This sort of definite criticism might be continued indefinitely. Thermodynamics should be a most important and valuable instrument of research; but the only possible reason today for urging a chemist to study thermodynamics is that we may some day find a man who can learn to handle his thermodynamics without losing his creative instincts. There have been such men. Van't Hoff was one, and the modern mathematical chemist speaks of him pityingly as not being very strong in thermodynamics. That is true; but van't Hoff knew that one must feed ideas into the thermodynamical machine if one is to get new results out of it. The men who improve on him have forgotten this essential point.

This screed is not directed against Mr. MacDougall's book but rather against the whole group of books of which this is merely one. One may however criticize the author legitimately for the way in which he has side-stepped the whole question of the degree of ionization. He not only does not commit himself at all; but he does not even tell the student that it is a vital problem. On p. 284 he says that in all methods of determining the degree of ionization "the correct interpretation of the results is conditioned by correct assumptions as to the nature of the substances present in the solution." On p. 286 he says that "if we assume that the degree of ionization of a solution of a binary electrolyte is given accurately by the relation . . . . .." That is hardly the accurate, logical and sufficiently rigorous application of the principles of science which we were

promised in the preface. The joke—or the sad part—of the thing is that the author has an improved dilution law and is therefore tremendously interested in the degree of ionization. *Wilder D. Bancroft*

Relativity, the Electron Theory and Gravitation. *By E. Cunningham. Second edition. 22 × 15 cm; pp. vii + 148. New York; Longmans, Green and Co., 1921. Price: $3.50.*—In the preface to the first edition (1915) the author says that the monograph is an attempt to set out as clearly and simply as possible the relation of the Principle of Relativity to the generally accepted Electron Theory, showing at what points the former is the natural and necessary complement of the latter. In the preface to the second edition (1920) he says: "The first edition of this book was published while the General Principle of Relativity was being worked out, before it seemed possible to arrive at any confirmation from observation. Shortly after, however, it was shown that the new Theory explained the motion of the perihelion of Mercury, and now the result of the Solar Eclipse expedition has clinched matters"

The book is divided into two parts, the first dealing with the special principle, and the second with the general principle of relativity. In the first part the chapters are entitled: the origin of the principle; the relativity of space and time; the relativity of the electromagnetic vectors; mechanics and the principle of relativity; Minkowski's four-dimension vectors In the second part the headings of the chapters are: the general theory, verification of Einstein's theory; further generalization, Weyl's theory of electricity

When discussing the Fitzgerald contraction, the author says, p. 55: "It is clear that there are two gaps in this argument. First, there is the obvious restriction that it must be assumed that, provided that the acceleration of the body is sufficiently slow, so as not to produce mechanical distortion, change of temperature or other disturbances, there is a *unique* configuration for a given grouping of electrons moving as a whole with a given velocity relative to the aether. This does not seem to offer any serious difficulty, though it must be remembered that the external configuration of a material body must be thought of as a statistical one; that is, in view of a probable kinetic constitution, to a fixed external configuration will correspond a multitude of rapidly changing distributions of electrons in the interior; but this will not be considered here. The more important point for discussion is that the correlation which has been shown to exist in the case of the 'field equations,' must be *assumed* to hold for all the other relations which play a part in determining the motions of the electrons.

"It has been remarked that it is enough for the purpose in hand to supplement the field equations by a hypothetical relation between the distribution of the charge that constitutes the electron and its velocity. If this is done, it must be a relation which maintains its form in the correlated moving system that we have built up. Since it is a purely geometrical relation it must be a relation which is invariant under, or is a consequence of, the fundamental transformation (A). Hence Lorentz's assumption that the electron, which is naturally thought of as symmetrical round a centre when it is at rest, is, when in motion, of spheroidal shape, being obtained from the spherical stationary electron by the simple application to it of the FitzGerald contraction. If this is not assumed, the correlation between the stationary and the moving system is not perfect, and we have

reason, therefore, for thinking that the desired contraction of the whole body will take place.

"Thus the whole explanation reduces to the formation of a conception of the electron, which really embodies the fact that we are trying to explain The origin of the contraction is left in obscurity. The conception is only arrived at by assuming the result of the experiment to be, not an accident arising out of the particular circumstances of the case, but inherent in the constitution of matter down to its most minute elements. In other words, *the formation of this conception of the electron is itself a direct application of the Principle of Relativity.*"

On p. 125 the author points out one weakness in Einstein's presentation. "In the preceding chapter the order of the argument has been mainly historical; the purpose has been to give a straight-forward account of Einstein's method and results. Before concluding, it is worth while however to recapitulate and to see the general lines upon which a radical reconstruction of physical theory must proceed. We shall see that even Einstein's generalized relativity is not the last word, and an attempt will be made to indicate the lines along which Weyl had shown that it is possible by a further step to give to electricity as natural a place as that accorded to gravitation in Einstein's theory Einstein himself has shown that it is possible to generalize the fundamental equations of electrical theory so that they have an invariant form, and are therefore consistent with the Principle of Relativity in the sense in which he uses the term But in his treatment the connection between the gravitational field and the geometry of the measure system is so intimate, while that between the electrical field and the measure system is so remote, that the fundamental place accorded to electricity in modern thought seems to be denied. In Weyl's theory it is completely restored, and gravitation and electricity rank together as two fundamental properties of matter, forming together the basis of all natural systems of measurement."

On page 144 the author gives a comparative survey of the situation at present. "It may be worth while to set down here a comparison of the conclusions from Newton's theory of dynamics, Einstein's restricted Principle of Relativity, Einstein's generalized theory, and finally Weyl's theory.

I. Newton —In the region of dynamics, of all possible co-ordinate systems there is a limited group for which the laws of motion have a particularly simple form. In any system of the group the path of a free particle is a straight line described uniformly.

II. Einstein, 1905.—*Restricted Principle of Relativity.*—In the region of dynamics and electro-dynamics, of all possible co-ordinate systems there is a limited group for which the laws are of precisely the same form. In any system of this group the path of a free particle is a straight line described uniformly, and light travels with constant velocity.

III. Einstein, 1915.—*General Principle of Relativity.*—In the region of gravitational phenomena, there is no restriction on the co-ordinate system but the measure-system is limited by the hypothesis (i) that the world-line of free particle is a direct line of the measure-system, (ii) that the curvature $G_{\mu\nu}$ may be identified with the presence of matter. The interval between two events is a fixed quantity within the appropriate measure-system.

IV. WEYL'S THEORY.—In electro-dynamic as in gravitational phenomena, there is no restriction on the co-ordinate system, and the measures of the interval between two events is not a definite quantity determined by the gravitation field. But of all possible measure-systems, there is one, or a limited group, in which the singular regions of the system are in exact correspondence with the regions in which matter or electricity are present.

"We conclude then that Einstein has satisfied the demand that nature itself shall not show any preference for any particular system of variables or co-ordinates by which we shall distinguish between events. Further, Weyl has made it clear that the laws of nature *do not supply* us with an absolute criterion of equality of intervals of space and time, except that of coincidence; in fact the idea of a definite measurable interval between two events has to some extent broken down. But we are not left with the conclusion that we may adopt an absolutely arbitrary system of measurement. There is necessarily one measure-system for a limited group, *within which there is complete relativity, of co-ordinates,* in which there is a particularly simple correspondence between the geometry of the system and nature; or in other words, for which the mathematical relations of nature take the simplest possible form.

"In the end we must admit therefore that the recognition of order in the sequences of events around us arises from an adjustment of mental machinery to the events. Just as we only recognize a star as a sharp point of light when the eye focusses the light on the retina, so we recognize a distinct order in the universe when we focus our measuring system properly. The eye has an infinity of ways of focussing itself so that the star produces a blurred image on the retina. So the mind may form many images of nature which are in a sense blurred, in which a distinct order is not perceptible. But the fact that the eye can produce a sharp image is enough both to determine our conception of the star, and to define what we mean by the proper focus for the star. So the problem of science is mainly to discover that mental focus in which nature gives us clear impressions of order. Einstein has shown that this may be done in a way far more comprehensive than had been thought possible. He has shown us that the required mental focus is to be attained without any introduction of metaphysical notions such as those of an asolbute space and time, or even of such a remnant of those notions as that light shall have a definite velocity the same at all points."

Wilder D. Bancroft

Anthracene and Anthraquinone. *By E. de Barry Barnett. 21 × 14 cm; pp. xi + 436. New York: D. Van Nostrand Company, 1921. Price: $6.00.*— It is over forty years since Auerbach published his book on "Anthracene and its Derivatives" and there have been many developments since then. Most important of them is that many of the valuable fast dyes belong in this category. The author has therefore given a fairly complete account of the work which has been published up to November 1920, on the derivatives of anthracene and anthraquinone, but not including such derivatives as chrysarobin, etc., which occur in nature and which are taken up in the book by Perkin and Everest entitled "Natural Organic Coloring Matters."

The subject is presented under the general headings: introduction; anthracene and its homologues; simple derivatives of anthracene; the anthraquinones

and dianthraquinonyls; anthrone, anthranol and allied products; anthraquinone and ring syntheses; the benzanthraquinones; the aldehydes, ketones and carboxylic acids; the nitro, nitroso, and halogen anthraquinones; the sulphonic acids, mercaptans and sulphides; the aminoanthraquinones and dianthraquinonylamines; the hydroxy and aminohydroxy anthraquinones and ethers; pyridine and quinoline derivatives; the acridones, xanthones, and thioxanthones; the benzanthrones; the cyclic azines and hydroazines; miscellaneous heterocyclic compounds; miscellaneous compounds.

The book is written primarily for the organic chemist; but there are many things in it which will appeal to the physical chemist. On p. 5 there are a few notes on dyeing. On p. 40 we note that reduction of anthracene with nickel and hydrogen does not necessarily give the same products as reduction with sodium amalgam. The changes of nitroxanthone, p. 60, should be studied. The colloid chemist will be interested in the technical method of powdering anthracene, p. 74, and the electrochemist in the use of ceric sulphate as a catalytic agent in oxidation, p. 75. Everybody will want to know why magnesium chloride increases the oxidation by sodium nitrate or chlorate, p. 75. Equilibrium relations should be determined for the compound obtained by reducing diphenylanthrone and treating with bromine, p. 104. On p 184 there are some remarks on dyeing with mercaptans.

The effect of boric acid is interesting, p. 243. "It appears that the nitro group is particularly easily replaced when it is in the *para-* position to a hydroxyl group, and under these circumstances the reaction is best carried out by heating with concentrated sulphuric acid in the presence of boric acid. The action of the boric acid in this case seems to be specific and not to be limited to protecting hydroxyl groups, as dinitroanthrarufin is stable towards concentrated sulphuric acid at 100° in the absence of boric acid, but in the presence of boric acid one nitro group is replaced by a hydroxyl group at this temperature, and at higher temperatures both are replaced. Dinitroanthrarufin disulphonic acid exhibits the same behaviour, as it is unaffected when heated for four hours at 150° with concentrated sulphuric acid in the absence of boric acid, but in the presence of boric acid one nitro group is easily replaced at 80°–90°, and both are replaced at 120°."

Boric acid is important in another capacity, p. 256. "When sulphuric acid acts as an oxidising agent it is, of course, reduced to sulphurous acid and this combines with the hydroxy compound produced to form a sulphite ester, this ester formation to some extent protecting the hydroxylated anthraquinone from destruction by further oxidation. Much more satisfactory results are obtained, however, by carrying out the oxidation in the presence of boric acid so that the boric ester is formed, and the same method is used when the oxidation is carried out with sulphuric acid and an oxidising agent. In any case when oxidation is complete the melt must be diluted and then boiled in order to hydrolyse the ester present. When the boric acid method is employed it is usual to add one part of crystallised boric acid to twenty parts of concentrated sulphuric acid, monohydrate, or oleum, and then to add the anthraquinone compound (one part) which it is desired to oxidise. The temperature is then maintained at a suitable point until examination of a sample shows that oxidation has gone as far as

desired, when the whole is cooled, diluted with water, boiled to hydrolyse the ester, and the hydroxy compound then filtered off.

"The addition of boric acid also slows down the reaction and, if sufficient is added, may even in some cases inhibit it altogether. This retarding action of boric acid is often very useful in preventing the reaction going too far. Thus the oxidation of alizarin with oleum of high concentration leads to quinalizarin in the absence of boric acid, but with the addition of a suitable amount of boric acid the reaction is so retarded that an almost quantitative yield of hydroxyanthrarufin can be obtained. In the same way the addition of boric acid renders it possible to oxidise chrysazin to 1.4.8-trihydroxyanthraquinone........

"Oxidation by means of sulphuric acid is a catalytic reaction and does not take place if chemically pure acids are used. When ordinary commercial acids are employed the small quantities of selenium present act as the catalyst:

$$SeO_2 = Se + O_2$$
$$Se + 2SO_3 = SeO_2 + 2SO_2$$

Oxidation by means of sulphuric acid is also facilitated by the presence of mercury compounds, and bromide is stated to facilitate attack by oleum, although this can hardly be regarded as a catalytic effect as bromination and hydroxylation take place simultaneously. Hydroxylation by oxidation with sulphuric acid or oleum often leads to the production of polyhydroxyanthraquinone sulphonic acids, but in many cases the sulphonic acid groups are readily removed by hydrolysis by heating the product with sulphuric acid of about 70 percent strength "

When alizarin is sulphonated in the presence of mercury, the products obtained are not the same as those which are formed in the absence of mercury, p. 278. "When Alizarin Blue and similarly constituted dyestuffs are allowed to remain in contact with concentrated aqueous solutions of sodium bisulphite for several days they combine with two molecules of the bisulphite and pass into water-soluble products which are very largely used in printing (Alizarin Blue S, Alizarin Green S, etc.). In text-books on tinctorial chemistry these soluble products are usually represented as being formed by union of the bisulphite with the cyclic carbonyl groups, but such a structure is very improbable as neither anthraquinone itself nor the hydroxyanthraquinones combine with bisulphite. Quinoline itself, however, forms an addition product with sodium bisulphite, and this resembles Alizarin Blue S by being decomposed by water at 60°. It is therefore probable that in the soluble dyes the bisulphite is united to the quinoline ring and not to the cyclic carbonyl groups."

Books of this sort are very important and this seems to be a good example of the type. *Wilder D. Bancroft*

Die Welt der vernachlässigten Dimensionen. *By Wolfgang Ostwald. Fifth and sixth editions. 23 × 16 cm; pp. xii + 253. Dresden and Leipzig, 1921. Price: 7 shillings.*—The fourth edition was reviewed last year (**24**, 592), The new edition—called the fifth and sixth—has about thirty-two pages more than the preceding one. Apparently the book sells extremely well in Germany; but one cannot help wondering how long it will be desirable to patch up lectures given in 1914 so that they will seem up to date. *Wilder D. Bancroft*

COAGULATION OF COLLOIDAL SOLUTIONS OF ARSENIOUS SULPHIDE BY ELECTROLYTES

BY E. F. BURTON AND E. D. MACINNES

In a paper by Burton and Bishop[1] on the Coagulative Power of Electrolytes for Sols of Arsenious Sulphide, Mastic and Copper in so far as this power changes with the concentration of the sol, the following results were obtained:

(1) For univalent ions the concentration of ion necessary to produce coagulation increases with decreasing concentration of the colloid—this increase being very rapid with low concentrations of the colloid.

(2) For divalent ions the concentration of ion necessary to produce coagulation is almost constant and independent of the concentration of the colloid.

(3) For trivalent ions the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid.

These results are in line with those already published by Mukherjee[2] and his co-workers and Kruyt and his collaborators.[3] Kruyt explains his results by adopting ideas suggested by Smoluchowski and Burger, viz., that coagulation depends on two sets of circumstances, first the probability of particles coming into collision with one another and, secondly, the likelihood of two particles adhering to one another when they do meet. The first probability depends fundamentally on the concentration of the sol and the second on the potential of the charge on the particle (see also Powis[4]).

The experiments described herewith were undertaken to get still more accurate and definite evidence on the coagula-

[1] Burton and Bishop: Jour. Phys. Chem., **24**, 701 (1920).

[2] Mukherjee: Jour. Am. Chem. Soc., **37**, 2024 (1915); Mukherjee and Sen: Jour. Chem. Soc., **115**, 462 (1919); **117**, 350 (1920).

[3] Kruyt: Koll. Zeit., **22**, 81 (1918); Kruyt and van der Speck: Ibid., **25**, page 1 (1919); Rec. trav. chim. Pays-Bas, **39**, 618 (1920).

[4] Powis: Zeit. phys. Chem., **89**, 186 (1915); Jour. Chem. Soc., **109**, 734 (1916).

tion of Arsenious Sulphide by using mono-, di,- tri-, and tetra-valent active ions. The results reported by Burton and Bishop have been completely confirmed.

Preparation of the Sol

The sol was prepared by bubbling hydrogen sulphide gas into a solution of arsenious oxide in water. Since the solubility of the oxide increases with the temperature, comparatively strong solutions of arsenious sulphide were obtained by boiling water, adding arsenious oxide, and bubbling in hydrogen sulphide gas. By bubbling in hydrogen sulphide gas before adding the oxide and continuously afterwards, one insures that at no time is arsenious acid present to any very great extent to act as a coagulating agent—the acid having been converted as soon as formed into arsenious sulphide. By this method colloidal solutions were prepared containing as high as .1096 mols. arsenious sulphide per litre.

The method of analysis of the solutions used was a co-precipitation method suggested by Professor Rogers. A 15 cc sample of the solution was dissolved by boiling with about 25 cc of concentrated nitric acid, a little hydrochloric acid and a pinch of potassium chlorate. About 2 grams of sodium phosphate was dissolved in a few cc of distilled water and added with a few cc of ammonia to the solution. Then all the phosphate and arsenate present was precipitated together by adding about 200 cc of magnesia mixture (the phosphate helping to bring down the arsenate). The phosphate and arsenate were precipitated as magnesium ammonium phosphate ($NH_4 MgPO_4 + 6H_2O$) and magnesium ammonium arsenate ($NH_4 MgAsO_4 + 6H_2O$), respectively—both coming down as fine white crystalline precipitates (Fresenius). The precipitates were allowed to settle over night and then filtered, washing out the flask with ammonia water (10%), the precipitates being less soluble in ammonia than in water. What remained in the flask was then dissolved in 40 cc of hydrochloric acid and 30 cc of water and the precipitate added,

including the filter paper—the whole being dissolved. The solution was then cooled and about 2 grams of potassium iodide dissolved in a few cc of water added, and the whole allowed to stand for a minute. Then 70 cc of water was added and the solution titrated against a standard solution of sodium thiosulphate, using starch as indicator.

The concentration of the sol obtained was .027 grams arsenious sulphide per cc of sol; this is the concentration A in the tables and figures.

Experimental

(1) Variation in the concentration of the electrolytic solution.

Mukherjee[1] found that using "different concentrations of the same electrolyte for titration of the same preparation of solution the quantities of electrolyte required are not in inverse ratio of the concentration of the electrolyte." This is a surprising result and certainly needed further testing. Experiments were first carried out in which the concentration of the electrolyte used was varied and the quantities of electrolyte of different strengths required to produce coagulation were determined. In these tests 10 cc of colloid were

TABLE I

Electrolytic Solution, A = 492.0 millimols aluminium chloride per litre

Concentration of electrolytic solution	Cc solution for coagulation	Concentration volume
A/1,000	.42	.00042
A/2,500	1.45	.00058
A/5,000	2.70	.00054
A/8,000	3.10	.00039
A/12,000	4.45	.00037
A/15,000	5.00	.00033
A/20,000	7.55	.00038
A/25,000	9.10	.00036
A/28,500	10.75	.00038
A/32,000	13.75	.00043

[1] Mukerjee: Jour. Am. Chem. Soc., **37**, 2024 (1915); Mukherjee and Sen: Jour. Chem. Soc., **115**, 462 (1912); **117**, 350 (1920).

taken, water and electrolyte added in the order named so that in each test the final volume was made up to 25 cc. As is shown in Table I and the curves of Figure 1, the volume of a given

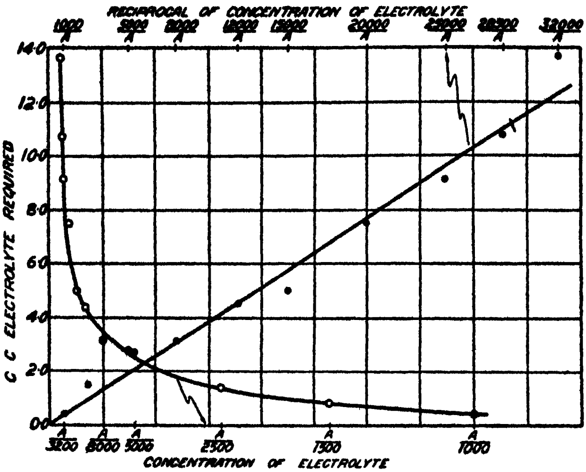


Fig. 1

electrolytic solution required for coagulation of a given amount of the disperse phase varies inversely as the concentration of the electrolytic solution, provided the final concentration of the colloid is kept constant.

(2) Coagulative power and concentration of the sol.

In making the following tests 10 cc of colloidal sol of determined concentration were put into a 75 cc test-tube. After preliminary tests, the strength of electrolyte used was such that about 10 cc of it caused coagulation within 10 hours. If b cc of electrolytic solution of strength x grams per cc were required to produce coagulation in a sample of 10 cc of sol, the final volume of the mixture would be $(10 + b)$ cc. If the concentration of the sol is y grams per cc then the final concentration of the colloid would be $\frac{10y}{10 + b}$ grams per cc and the final concentration of the electrolyte would be $\frac{b.\,x}{10 + b}$ grams per cc.

Experiments were carried out with the following electrolytes:

Univalent cations:	Potassium Chloride
	Lithium Chloride
Divalent cations:	Magnesium chloride
	Barium chloride
Trivalent cations:	Aluminium chloride
	Lanthanum sulphate
Tetravalent cations:	Cerium nitrate
	Zirconium chloride

The results are given in Tables 2 to 5 and illustrated in Figures 2, 3, and 4. In the tables and figures A means the maximum concentration of arsenious sulphide per cc of final solution. New samples of sol generally of concentration $^3/_4$, $^1/_2$, $^1/_4$, and $^1/_8$ of A were used in successive experiments.

TABLE 2

Univalent Ions

Potassium chloride conc. 487.5 millimols per litre			Lithium chloride 384.0 millimols per litre		
Final conc. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre	Final conc. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre
A	4.7	91.6	A	6.2	95.2
3A/4	4.4	85.8	3A/4	6.5	99.8
A/2	5.2	101.4	A/2.3	7.4	113.7
A/4	6.9	134.5	A/4	9.3	142.9
A/8	7.2	140.4	A/8	11.5	176.6

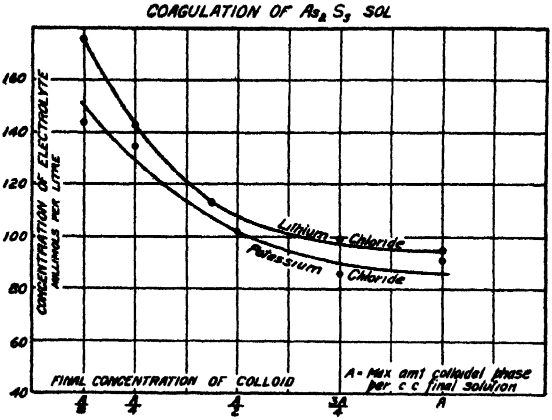


Fig. 2

TABLE 3

Divalent Ions

Magnesium chloride conc. 4.74 millimols per litre			Barium chloride 4.23 millimols per litre		
Final conc. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre	Final conc. sol.	Cc electrolyte required for coagulation	Conc. elec. in final mixture, millimols per litre
A	9.3	1.76	A	10.0	1.69
3A/4	9.2	1.74	3A/4	9.3	1.57
A/2.5	8.8	1.67	A/2.4	8.1	1.37
A/4	8.7	1.65	A/4	8.3	1.41
A/8	9.8	1.86	A/8	8.2	1.39

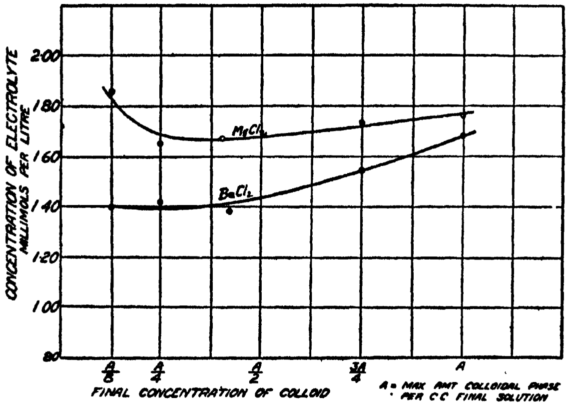


Fig 3

TABLE 4

Trivalent Ions

Aluminium chloride conc. .0615 millimols per litre			Lanthanum sulphate .134 millimols per litre		
Final conc. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre	Final conc. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre
A	11.9	.0293	A	11.5	.0621
3A/4	9.7	.0239	3A/4	9.5	.0513
A/2.1	6.3	.0155	A/2.2	7.1	.0383
A/4	4.1	.0101	A/4	6.0	.0324
A/8	2.8	.0069	A/8	5.8	.0313

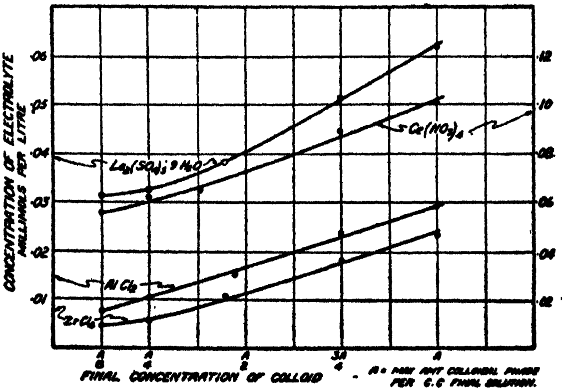


Fig. 4

Table 5

Tetravalent Ions

Zirconium chloride conc. .0378 Millimols per litre			Cerium nitrate .0166 millimols per litre		
Final concn. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre	Final conc. sol.	Cc electrolyte required for coagulation	Conc. electrolyte in final mixture, millimols per litre
A	15.5*	.0234	A	15.2*	.101
3A/4	12.0	.0181	3A/4	13.3	.089
A/2.2	7.1	.0107	A/2.6	9.8	.065
A/4	3.75	.0057	A/4	9.3	.062
A/8	3.0	.0045	A/8	8.5	.057

* This represents the first coagulation produced by these electrolytes. Addition of greater amounts produced a stabilizing effect: this shows the existence of what has been called a coagulation zone.

Conclusion

These results bear out exactly the former experiments performed by Burton and Bishop already referred to in the first paragraph of this paper. It may be worth noting that the curve for barium chloride shows a tendency toward the trivalent curve represented by aluminium chloride; the barium ion is noted as one of the most powerful of the divalent ions. In addition we have the curves representing tetravalent ion, Zr showing the characteristics which we should have expected, while cerium seems to act similarly to trivalent ions. In conclusion we wish to express our thanks to Professor Rogers and the Department of Chemistry for advice and gift of the rarer salts.

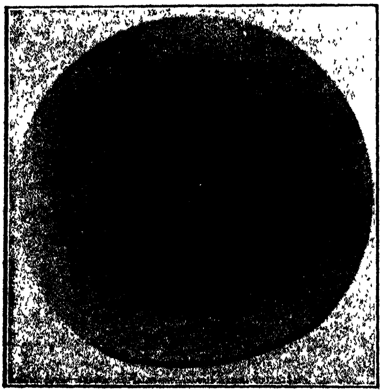
NOTE ON LIESEGANG RINGS IN STRAINED GEL

BY E. F. BURTON AND G. C. BELL

The article on the Liesegang Phenomenon by Hatschek in the Second Report on Colloid Chemistry issued by the British Association Committee, closes with these words: "The experimental reproduction and elucidation of natural periodic structures should for a long time to come be one of the most fruitful fields for applied colloid chemistry. It seems probable that investigation will have to be extended to gels made anisotropic by stress, since it is evident that most of the gel-like constituents of organisms are in such a condition, at least during long periods."

About the time that this was written experiments were being carried on here on various phases of this phenomenon, and in particular the formation of the Liesegang rings in stretched gelatine was tried.

The gelatine film, impregnated with potassium chromate in the usual way, was formed on a sheet of thin rubber instead of on a glass slide. The rubber was held between two roller clamps so that it could be stretched parallel to a given direction. After the film had been stretched thus and while still stretched, the drop of silver nitrate solution was allowed to dro pon the central portion. The accompanying photograph gives the appearance of the resulting rings. The longer dimension of the ellipse is in the direction of the stretching force. This arrangement is probably just what one might expect but it seems to be one experiment along the line suggested by Hatschek.



THE FREEZING-POINT DIAGRAM OF THE SYSTEM PHENOL-WATER[1]

BY F. H. RHODES AND A. L. MARKLEY

Several authorities have stated that phenol forms one (or more) definite hydrates while other investigators have been unable to obtain any evidence of the existence of any definite hydrate. The first description of a definite hydrate of phenol appears in an article by F. C. Calvert[2] in 1865. Calvert stated that when a mixture of four parts of phenol and one part water of water is cooled to 4° C rhombic crystals of phenol hydrate are formed. On further examination, the hydrate crystals were found to melt at 16° C and have the formula $2C_6H_5OH.H_2O$. At the Paris Exhibition of 1867, F. Crace Calvert and Co., and Charles Lowe and Co.[3] exhibited, among other products, a sample of this hydrate of phenol. In the same year, Calvert[4] stated that by removing from this hydrate the equivalent of water which it contains, phenol is obtained in its purest state."

In 1874, Charles Lowe and John Gill[5] patented the "separation of phenol from the cresylic acids and other liquid tar acids—by the formation and separation of hydrated carbolic acid crystals and from the mother liquor." In their patent they stated that the temperature at which the hydrate crystals formed was between 15° F and 56° F. Further details of the purification process of Lowe and Gill were given by Marzell.[6]

Alexejeff[7] tried to prepare phenol hydrate by the method described by Lowe, but was unable to obtain any indication

[1] Contribution from the Department of Chemistry of Cornell University.
[2] F. C. Calvert: Jour. Chem. Soc., **18**, 66 (1865).
[3] Chem. News, **16**, 57 (1867).
[4] Calvert: Chem. News, **16**, 297 (1867).
[5] Chem. News, **31**, 52 (1875); Brit. Pat. No. 1435 (1874).
[6] Marzell: Chem. News, **37**, 105 (1878).
[7] Alexejeff: Jour. Soc. Chem. Ind., **1**, 397 (1882).

of the existence of a definite compound. On the basis of his results, he concluded that the hydrate described by previous investigators was only a mixture of phenol and water. Paternò and Ampola[1] were also unable to obtain any evidence of the existence of a definite hydrate of phenol.

Smits and Maarse[2] found that phenol hydrate is not easily formed when a mixture of phenol and water is cooled. Under ordinary conditions, supercooling takes place and solid anhydrous phenol is obtained. By cooling a mixture of phenol and water in a bath of solid carbon dioxide and alcohol, however, crystals of a hydrate of the formula $2C_6H_5OH.H_2O$ were obtained.

In view of the rather meagre and contradictory nature of the previously published information concerning the existence and properties of phenol hydrate, this present investigation of the freezing-point curve of the system phenol: water was undertaken.

Experimental

The phenol used in this work was prepared from a sample of refined natural phenol which was presented to this laboratory by the Chemical Department of the Barrett Company. The original material was dissolved in a twenty-five percent solution of sodium hydroxide, and steam was passed through the resulting solution to remove all traces of oil. The solution was then cooled and neutralized with a twenty percent solution of sulphuric acid. The resulting phenol layer was distilled, and the distillate was redistilled through an efficient fractionating column. Only that portion of the distillate which had a melting point of 40.4° C or above was collected for use in the subsequent experiments. The distillate was collected directly in large test-tubes, 8 in. x $1^1/_4$ in., which had previously been dried and weighed. from nine to sixty grams of phenol was collected in each tube. Each tube

[1] Paternò and Ampola: Gazz. chim. ital., **27**, 481 (1897).
[2] Smits and Maarse: Ver. Kon. Akad. Wet., **20**, 100 (1911–12).

was then closed with a cork stopper covered with tin-foil, weighed, and stored in a desiccator over phosphorus pentoxide.

In determining the melting points of mixtures of phenol and water, the following procedure was adopted:

To a tube containing a known amount of the pure phenol was added a known amount of pure water, sufficient to give the desired mixture. The tube was then suspended, by means of a cork stopper, in a larger tube which was immersed in a cooling bath (cold water, ice, or ice and salt) at a temperature slightly below the estimated freezing point of the mixture. The stopper in the sample tube was replaced by a cork carrying a thermometer and a glass stirrer, and the sample was allowed to cool slowly and with constant stirring. As the estimated melting point was approached, the mixture was "seeded" by adding small crystals of solid phenol or phenol hydrate. The highest temperature at which permanent crystals could be obtained was taken as the freezing point of the mixture. Each determination was repeated several times to insure the elimination of errors due to supercooling or to error in obtaining the exact phenol-water ratio in the sample.

The thermometer used in this work was a "Tycos" nitrogen-filled mercurial thermometer, graduated to read directly to 0.1° C. The thermometer was calibrated before use and was found to read correctly.

The results obtained are shown by the following tables:

TABLE I

Stable Equilibria

Water, %	Temp., °C	
0	40.8	Melting point of phenol
2	33.0	Solid phenol in equilibrium with liquid phenol containing phenol hydrate in solution
3	29.3	
5	23.1	
8	16.2	
8.16	15.9	
8.25	15.8	Eutectic phenol and phenol hydrate
8.41	15.9	Phenol hydrate in equilibrium with liquid hydrate containing phenol
8.56	15.9	
8.74	15.9	Melting point of phenol hydrate

Table I (*Continued*)

9.00	15.9		Solid hydrate in equilibrium with liquid hydrate containing water
10.	15.75		
11.	15.45		
12.	15.15		
14.	14.40		
16.	14.00		
18.	13.30		
20.	13.00		
22.	12.70		
24.	12.40		
26.	12.30		
27.	12.20		Two liquid layers appear
35.	12.20	C.	
70.	12.20	0.85	Ice, solid hydrate, and water containing dissolved hydrate
75.	12.20	0.85	
88.	12.20	0.85	
91.	12.20	0.85	
95.		0.85	—Eutectic, hydrate, ice, solution
97.		0.6	Ice, in equilibrium with solution of hydrate in water
98.		0.45	
98.5		0.35	
100.		0.00	—Melting point pure water

Table II

Metastable Equilibria

Water, %	Temp., C		
9	14.1		Solid phenol in metastable equilibrium with liquid phenol containing water
12	9.3		
15	6.2		
18	4.2		
20	3.1		
22	2.3		
23	2.0		
24	1.8		
25	1.7		Two liquid layers appear
35	1.7		
50	1.7	C.	
75	1.7	1.2	Ice in equilibrium with solid phenol and water containing dissolved phenol
80	1.7	1.2	
88	1.7	1.2	
90	1.7	1.2	
91	1.1	1.2	
92	0.9	1.2	
92.5	0.6	1.2	
93	0.0	1.2	
93.5		1.2	— Eutectic, ice, solid phenol, solution

TABLE II (*Continued*)

94	1.1	Ice in equilibrium with solution of phenol in water
95	1.0	
100	0.0—	Melting point pure water

These results are shown graphically by the accompanying curve.

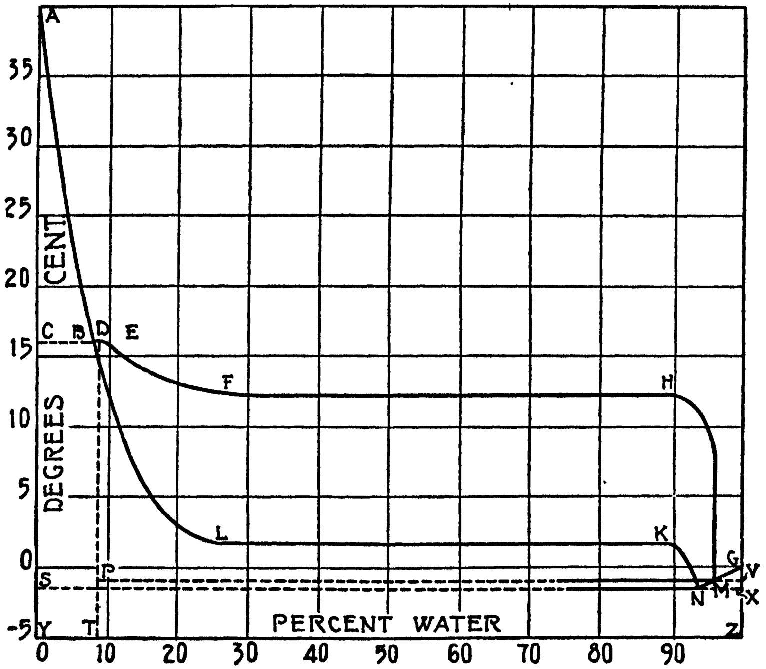


Fig. 1
Phenol and Water

Discussion

From these data it is apparent that we have to deal with two distinct systems:

(1) The system of stable equilibria between phenol, phenol hydrate and water, and

(2) The system of metastable equilibria between anhydrous phenol and water.

In order to simplify the discussion, each system will be considered separately.

The system of stable equilibria is represented by the curves ABDFHMG and PM. The point A represents the melting point of the purified anhydrous phenol. It is worthy of note that the melting point of the carefully purified phenol was found to be 40.8° C. The values given in most of the chemical handbooks vary between 42° C and 43° C. In this present investigation, as well as in previous unpublished work done by one of us, careful attempts to prepare pure phenol from both the natural and synthetic product gave a purified phenol which melted at 40.8° C. We therefore consider this to be the true melting point of phenol.

The addition of small amount of water lowers the melting point of phenol very rapidly. The curve AB represents the (stable) equilibria between solid phenol and solution. At point B (8.25% water, 15.8° C) the eutectic between phenol and phenol hydrate is reached. The further addition of water increases the melting point until point D, the melting point of the pure hydrate is attained. This hydrate contains 8.74 percent of water, corresponding to the formula $2C_6H_5OH.H_2O$, and melts at 15.9° C. The curve BD represents the equilibria between solid hydrate and solution rich in phenol.

The further addition of water lowers the melting point again until point F (27% water, 12.2° C) is reached. At this point two liquid phases appear, liquid phenol saturated with water, and water saturated with phenol hydrate. The addition of water beyond this amount merely varies the relative proportions of the two liquid layers and does not affect the freezing point of the phenol hydrate layer. At point H (91% water, 12.2° C) there is present enough water to hold in solution (at 12.2° C) all of the phenol hydrate. A further increase in the amount of water prevents the formation of a separate liquid layer of phenol hydrate, and lowers the freezing point rapidly to the eutectic M. The curve HM, therefore represents the equilibria between solid phenol hydrate and solution of phenol hydrate in water.

M (95% water, −0.85° C) is the eutectic at which solid hydrate is in equilibrium with ice and solution. The line

MG represents the temperatures at which ice is in equilibrium with solution.

Thus, in thes ystem phenol–phenol hydrate–water, we have the following fields of stability:

Field	Phases
ABC	Phenol crystals, solution,
BCYT	Phenol crystals, hydrate crystals,
DEB	Hydrate crystals, solution,
DPMHF	Hydrate crystals, solution of hydrate in water,
MGV	Ice, solution,
PTZV	Ice, hydrate crystals.

In addition to this series of stable equilibria, there exists a series of metastable equilibria represented bythe curve BLKNG. The curve BL, which is the continuation of the curve AB represents the metastable equilibria between solid phenol and a solution of water in phenol. At L (25% water, 1.7° C) two liquid phases first appear:

(1) a saturated solution of phenol in water, and
(2) a saturated solution of water in phenol.

The further addition of water beyond this point results merely in a change in the relative amount of the two layers, the freezing point of the phenol layer remaining constant at 1. 7° C.

At point K(90% water, 1.7° C) the amount of phenol present is just sufficient to saturate the water. The addition of more than ninety percent of water causes the phenol layer to disappear, and the freezing point drops sharply to point N (93.5% water, −1.2° C). This point is the eutectic at which solid phenol and ice coexist in (metastable) equilibrium with a saturated solution of phenol in water The further addition of water causes the freezing point to rise, as indicated by line NG, representing the equilibria between ice and solution.

Thus in the system phenol–water we have the following fields of equilibrium.

Field	Phases
ABLKNSC	Solid phenol, solution. (In this field, the area ABC represents stable equilibria. In all of the remainder of the field the solid phenol is metastable.)
NGX	Ice, solution. (Of this field, portion MGV is stable, while NMVX is metastable.)
SXZY	Solid phenol, ice-metastable throughout.

In these experiments it was found that when a liquid mixture of phenol and water was cooled by any of the ordinary refrigerating agents (cold water, ice, or ice and salt) no formation of hydrate crystals occurred. In every case the solid phase which separated was either solid phenol (from solutions containing less than 93.5% water) or ice (from solutions containing more than 93.5% water). No crystals of phenol hydrate could be obtained even when mixtures of phenol and water were allowed to stand overnight at $-20°$ C. Hydrate crystals were originally obtained only by the method suggested by Smits and Maarse, i.e., by cooling a solution of fifteen percent of water in phenol for one hour to a temperature of $-78°$ C, using as a refrigerating agent a mixture of solid carbon dioxide and alcohol. Points on the stable curve (BDEFHM) were then easily determined by seeding the proper mixtures, at the proper temperatures, with small crystals from this lot of hydrate. By this procedure it was found possible to avoid supercooling and suspended transformation.

Summary

The complete freezing point diagram of the system phenol–water has been determined. Phenol forms a definite hydrate, $2C_6H_,OH.H_2O$, melting at 15.9° C, and forming eutectics with anhydrous phenol and with ice, respectively.

Because of the tendency toward suspended transformation, the solid phase which ordinarily appears when a mixture of phenol and water is cooled is the metastable anhydrous phenol. Hydrate crystals were obtained only by seeding with hydrate or by cooling to very low temperatures.

Ithaca, New York

THE RELATIVE DENSITIES OF ALKALI-METAL AMALGAMS AND MERCURY. II*

BY EDGAR C. BAIN AND JAMES R. WITHROW

This work (1) furnishes experimental confirmation of the deductions made upon this subject in the previous paper by one of the authors.[1] (2) It supplies visual and analytical proof of the relative densities of solid alkali-metal amalgams and the liquid or solution phase in contact. (3) It demonstrates that solid amalgams are specifically lighter than their liquid contact phase in the case of Kerp's method of production as well as other methods. (4) It shows the real nature of "oily" and "pasty" amalgams. (5) It studies the maximum concentration of potassium in amalgams produced by electrolysis of saturated KCl solution. (6) It studies the preparation of calcium and ammonium amalgams.

Historical

The question of the relative densities of solid amalgams and their liquid amalgam phases in contact has attracted considerable attention. In describing a method for continuously producing solid amalgams, Kerp[2] gives an illustration showing the final product as separating by virtue of difference in density into solid and liquid amalgam, and has labelled the *lower* phase in his illustration as the solid amalgam. This illustration has been reproduced by Abegg.[3] This ignores the early work of Robert Hare[4] which showed that ammonium amalgam when frozen floats on mercury. The later work of Shepherd,[5] G. McP. Smith and Withrow,[6] Whiting,[7] and

*Contribution from the Chemical Laboratory of the Ohio State University.

[1] Jour. Phys. Chem., **20**, 529 (1916).

[2] Zeit. anorg. Chem., **17**, 300 (1898).

[3] Handbuch anorg. Chemie., **2** II, 579 (1905).

[4] Edgar F. Smith: "Life of Robert Hare," page 313 (1917).

[5] Jour. Phys. Chem., **7**, 29 (1903).

[6] Jour. Am. Chem. Soc., **29**, 321 (1907).

[7] Trans. Am. Electrochem. Soc., **17**, 327 (1912).

Withrow,[1] furnishes reasonably clear evidence that at least some alkali amalgams appear lighter than mercury or their liquid phase in contact. The proof of this however is not complete, but the evidence seems strong. The object of this work was to acquire experimental proof.

Familiarity with the physical and chemical properties of two phase amalgams will soon convince one of the difficulty of solving this problem. Specific gravity values such as may be calculated from results recorded by Maey[2] show the heaviest solid potassium amalgam to have the density of 13.3707. Mercury has a density of 13.595. Maey's tables, when inspected and recalculated, show no solid amalgam heavier than liquid amalgam or mercury. While a continuation of the work of Maey is desirable, the purification and preservation of amalgam for specific gravity determinations presents numerous difficulties and is not a satisfactory method for solving the question before us, since a comparison is wanted merely between the solid phase and its liquid phase in contact. The industrial aspects of this problem have already been pointed out in the previous paper.[3]

Amalgam Preparation

The Shepherd method[4] (G. McP. Smith and Withrow,[5] Frank and Withrow[6]) was used with a porous cup and saturated solution of KCl as electrolyte. A 4 x 8 cm. porous cup was boiled in KCl solution until crystals formed on the inside which could be washed down. Two hundred grams of mercury were placed in the porous cup and some 20 to 30 grams of dry KCl scattered on its surface. Four to six amperes current flowed at five to seven volts for two hours. Con-

[1] Loc. cit.
[2] Zeit. phys. Chem., **29,** 128 (1899).
[3] Loc. cit.
[4] Jour. Phys. Chem., **7,** 29 (1903).
[5] Loc. cit.
[6] Jour. Am. Chem. Soc., **42,** 671 (1920).

siderable heating took place and water was frequently added to the beaker, also, some KCl from time to time. Only a slight moistening of the KCl crystals in the cup took place due to endosmosis, in agreement with the observations of Frank and Withrow.[1] When cooled somewhat from the temperature inside the cup, 70° to 80° C, the amalgam produced became very hard. When broken, it was an aggregate of many large crystal grains.

The directions of Smith and Bennett[2] were followed in the preparation of sodium amalgam. The cathode and electrolyte container had a diameter of 5.5 cm and the anode presented approximately 8.5 sq cm surface and was quite close to the surface of the mercury. Two hours at a rate of four to six amperes with the cell surrounded by water in a larger glass dish produced a thick pasty or mealy product. The NaCl electrolyte soon reached a temperature of 70° to 80° C and remained so. The amalgam became rigid when cooled to tap water temperature, but crumbled when handled.

This method was also employed to make some potassium amalgam. In 75 minutes a current of 4 to 6 amperes, at 7 to 9 volts, produced about 250 grams of amalgam which, when allowed to cool down slowly, formed very large cubes, some with 5 mm edges, and finally became rigid so that it was removed from the beaker in one block. The same cell was employed as in the case of sodium amalgam and will be known in this work as the standard cell, since all further work was done in it. During these preparations the salt crept and spattered up to the edges of the beaker and electrode supports, and down the outsides, but no great inconvenience resulted from this behavior. So long as the current did not increase above 5 to 6 amperes the bath did not reach boiling temperature, but it did evaporate considerably even at 85° C.

[1] Loc. cit.

[2] Jour. Am. Chem. Soc., **31**, 301 (1909).

Determination of Relative Densities

Since only relative densities and not absolute values were sought, consideration of a method involving the measurement of the volume of the amalgam produced from a known volume of mercury appeared worth while. Even the simplest apparatus for accomplishing this however, becomes evidently impracticable, because of difficulties from incorporation of moisture, salt, products of decomposition, and gases, which cannot be seen by the eye, in a given solid amalgam. Pipetting samples from various points in a mixture also was found unsatisfactory. When one considers that water may be drawn out along with mercury over which it has been poured, at a point several centimeters below the surface of the mercury, this last method, and ordinary separatory funnel principles cannot be used with certainty.

Apparatus.—For the examination of a mixture of solid and liquid amalgam free from contamination, a simple apparatus was designed. It consisted of cylinders of glass about 2.5 cm internal diameter with ground flanged tops, resurfaced by a fine abrasive and set into large plaster of paris blocks. One cylinder was cut off 5 cm from the top. The plaster of paris continued the surface of the ground flanged tops, for the cylinder flanges were inverted upon a glass plate, in casting, to form the bottom of the mold. When the ground flanges with their continuous plaster of paris surface of considerable area were placed to face upon each other, the two cylinders formed one continuous vertical cylinder reinforced at the flanged joint by a split plaster of paris block, sufficiently large so that sliding the one block upon the other had the effect of pulling the top section of the cylinder completely out of alignment and connection with the lower section. The lower cylinder was partially filled with plaster of paris to avoid the necessity of a large sample of material.

Procedure.—The process for using this device was also simple. The amalgam as produced was prepared as for analysis, then poured into the double cylinder and vigorously

stirred up and down and then allowed to rest for a few minutes. The whole was then placed in a large evaporating dish and the top slowly and evenly slid upon the lower section. Then by holding the top and bottom plaster of paris blocks together the mass could be emptied from the top, then with the top removed the contents of the lower could be separately emptied into another container for examination and analysis. The physical nature, alone, of the top and bottom portions gave the solution of the problem.

The simplicity of this procedure eliminates tedious purifications, weighings, or volumetric measurements, which could easily be discounted. In each case, for additional information, the separated portions were analyzed. The method of analysis was that employed by Smith and Withrow (*Loc. cit.*)

Experimental Data

Typical analyses of upper and lower phase amalgams follow:

Run No.	Amalgam alkali	Percent alkali Top	Bottom
1	K	1.48	1.46
2	K	0.76	0.47
3	K	0 74	0.49
4	K	1.12	0.49
5	K	1.18	0.86

In run No. 1, 800 to 900 grams of amalgam were made using the standard cell. In 90 minutes the mass in the cell seemed somewhat thick and was poured out, washed in distilled water, dried with filter paper and put into the separator. The mass was so stiff when cool that it had to be scraped into the separator. After standing a short time the top was slipped over. The amalgam did not pour easily from either section. So far as could be judged the parts were alike in physical properties. The chemical analysis also showed them to be practically the same. The run had obviously been continued too long.

Run No. 2 was made under similar conditions but stopped

much sooner. In the separator, the upper portion, after 4 to 5 minutes standing would just barely pour out, while the lower was very like pure mercury, except for a few rather small crystals. The chemical analysis showed the higher potassium content to be in the upper portion. In other words, the solid amalgam floated at the top and did not sink as shown in the record of Kerp and Abegg.

Run No. 3 used only slightly shorter time and it gave results similar to number 2. A rather longer run—4—was made and fifteen minutes allowed for flotation. In this case some 900 or 1000 g of mercury were used and when the top was slipped over on the lower cylinder block the crystals had matted so at the top that 327 g of crystals stuck in the top of the cylinder in a *solid mass* and from the space *below* this, and above the line of separation, there drained out 215 g of amalgam—liquid and solid. The portion in the lower block was entirely liquid so far as could be detected by pouring through a small aperture. This gave a striking visible demonstration that solid amalgam floats.

The portion of the upper section draining away from the solid mass of crystals at the top contained 0.59 % K. Chemical analysis again showed the higher K content amalgam to be in the upper section.

This run was so conclusive that a few attempts were made to get such a proportion of solid and liquid that the top would just be almost rigid and the lower part just all liquid. Two runs were made in which this situation was surprisingly nearly realized in that the contents of the upper part of separator would stand for several minutes rigid in the casserole like ingots of cast metal, while the lower portion was contaminated with only a few coarser crystals. Analyses were not made.

It was thought advisable now to make a few brief tests to see if sodium amalgam possessed similar properties. In general, sodium amalgam crystallizes in much smaller crystals and hence separation is slower. But substantially the results are the same as for potassium. Several runs were made

with very satisfactory results, in that the top portion was quite thick with fine crystals.

Verification of Results in the Case of the Kerp Method

Although there was no reason whatever for suspecting that amalgams produced by the method just described, possessing peculiar reversals of properties at variance with those produced by the continuous method of Kerp, nevertheless, amalgams were made by the Kerp method and examined. As nearly as possible there were embodied in a complicated apparatus, all the features of Kerp's apparatus. In No. 5, with an E. M. F. of nearly 25 volts applied for 105 minutes nearly 1200 g of "slushy" amalgam were produced. Toward the end of the run the amalgam had a tendency to become more and more "oily" and "pasty" and adherent toward glass, and finally in the upper reservoir coarse crystals could be felt and at last some crystals clogged the fine aperture, whereupon the run ended. The amalgam was poured into the separator and stirred up and down vigorously, it being a few degrees above room temperature. In about twenty minutes it had cooled to room temperature and separation was made. The upper section slid out of the cylinder and stood up perfectly in the dish like cast tin. The *lower section* contained some few crystals but was essentially all liquid. Moreover, the upper portion had a potassium content on analysis which was markedly higher than the lower portion.

"Oily" and "Pasty" Amalgams.—The consistency of the more mobile of the amalgams is thick, oily or pastelike. To investigate this property some amalgams were made by short runs with the usual methods. They had just such characteristics and were permitted after washing and drying to stand some little time in closed vessels. Then the amalgams were subjected to filtration through chamois skin in a Gooch funnel and the filtrates examined in dry glassware. These were not "oily" or "pasty" to any extent but seemingly as mobile as mercury itself and only slightly adherent to glass. The filter when examined showed a compact deposit of very fine silver-white crystals of somewhat graphitic feel when

rubbed between chamois. The yield was higher for the "thicker" amalgams.

A composite sample of filtrates showed a concentration of Na equal to 0.74%. Sodium amalgams were chosen because they exhibit these characteristics best. Evidently "oily" or "pasty" amalgams are due to fineness of amalgam crystal grain.

The Maximum Concentration of Potassium Obtainable in an Amalgam Produced by Electrolysis of a Saturated KCl Solution.—The standard electrolytic cell was used and a heavy current passed through for various periods to see if a limiting value could be obtained. The first few experiments were sufficient to demonstrate that a cool electrolyte would produce a solid block of amalgam in the cell which could not of course be enriched to any extent on account of the impenetrability to newly discharged potassium ions. The solutions were permitted to boil under the heavy current, which took place at a temperature of 108° C.

The results of these experiments were as follows:

Mercury, grams	Voltage	Current, amperes	Time, minutes	Percent, potassium
257.3	9–12	12–15	40	1.90
207.4	9–12	12–15	85	2.00
223.3	9–12	12–15	125	2.30
279.0		18–22	145	2.14
250.0		18–22	175	2.31

From these results it would seem that 2.31% potassium was a maximum. There is some loss inevitable in the washing of the amalgam and a safe estimate of the true concentration would be not greater than 2.35%. This is very nearly the content of Hg_8K (2.38%) and shows that there is little likelihood that Kerp could have prepared a heavier amalgam.

In these runs it was noticed that after forty to sixty minutes the odor of evolved chlorine was not noticeable, and in a short time the vapors of the cell could be inhaled with no irritation and only a faint suggestion of the "hypo-

chlorite" smell. It was suggestive of the smell of bleaching powder on the skin. It was thought that this cessation marked with reasonable closeness the saturation of the mercury with the alkali metal. Time did not permit investigating whether the alkali had run out or the hydroxyl concentration was taking care of the halogen at this point.

Ammonium Amalgam.—No one in the literature speaks of having obtained a crystalline ammonium amalgam, although Hare[1] does refer to a frozen ammonium amalgam and Moissan[2] says that ammonium amalgam produced and washed at low temperatures increases in volume from 15–20 times when the temperature rises from —80° C to +15° C. We made a few runs to see if our technique would produce a crystalline amalgam electrolytically. The method used was much the same as that used by J. Schroeder[3] and was as follows: A block of NH_4Cl (such as tinners use) was chiselled into a small cup and surrounded in a beaker with saturated NH_4Cl solution. Mercury was placed in the cup—about 10 grams—and a platinum connector inserted. A large platinum electrode formed the anode. Voluminous ammonium amalgam was produced copiously with about 10 volts E. M. F. It foamed up in a continuous, loose, ropelike mass. Much less mercury was used another time but the only difference noted was that the amalgam did not overflow the container. It was concluded, therefore, that a crystalline ammonium amalgam could not be produced by this method. The product appeared more like the "oily" or "pasty" amalgams just described than like crystalline amalgams.

Calcium Amalgam.—It was attempted to produce calcium amalgam by using a fairly strongly acid solution of calcium acetate and acetic acid with high current density. After some forty minutes the mercury showed some alkaline-earth content, but it gave only a minute's effervescence in

[1] Loc. cit.
[2] Bull. Soc. chim. Paris, (3) **27**, 717 (1902).
[3] Jour. prakt. Chem., **77**, 271 (1908).

acid solution. No trouble however was encountered from $Ca(OH)_2$ precipitation as mentioned by other investigators. Carrying this out at low temperatures may solve this hitherto unsatisfactory preparation.

Summary

1. Solid alkali amalgams float on the "mother liquor," and do not sink in it as alleged by Kerp and Abegg.

2. The method of Kerp produces sodium and potassium amalgams which are like amalgams produced by the other methods in that the solid is lighter than the liquid.

3. "Oily" and "pasty" consistencies in liquid (?) amalgams are due to fine crystals incorporated in the liquid.

4. By electrolysis potassium amalgams with concentrations up to 2.31% were obtained.

5. No difficulties except collection and preservation of a very spongy mass confront the investigator who would produce ammonium amalgam by electrolysis of NH_4Cl. Crystalline ammonium amalgams were not produced.

6. Acidified $Ca(C_2H_3O_2)_2$ with high current does not form a very satisfactory solution for the electrolyte of a calcium-amalgam cell, but yet does really produce a little of the amalgam, and offers hope for the elimination of the $Ca(OH_2)$ evil.

The authors thank Mr. Lawrence E. Stout, Assistant in this laboratory for his help in assembling these notes.

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REACTIONS IN FUSED SALT MEDIA—I. A STUDY OF THE BASIC LEAD CHROMATES

BY J. F. G. HICKS

Heintz,[1] working in this laboratory, prepared lead chromate and lead carbonate in a reaction-medium, or vehicle, of fused sodium chlorid. It was suggested[2] that the writer continue the investigation with a view to studying the mechanism of these fusion-reactions. The basic lead chromates offered an interesting problem, and were studied in some detail. Some analogies to hydrolysis have been noted, and the investigation would seem to throw some light on the mechanism of formation of certain "basic" salts.

The experimental work herein recorded is admittedly preliminary, and certain phases of the investigation are still in progress. With two possible exceptions ($PbO.4PbCrO_4$ and $PbCrO_4.4PbO$) no new compounds are noted, nor was it originally intended to prepare any. However, it is thought that the mechanism of such reactions may be of interest.

Apparatus.—A "surface-combustion" furnace[3] was used for the rapid fusion of sodium chlorid (m. p., 820°) where such fusions were of larger volume than 50 cc. No special heating-device was necessary for smaller fusions or for those of lower melting-points. Cooling-curve data were obtained by the use of a Pt/Pt-Rh thermo-couple.

Materials.—Sodium chlorid was first used as a solvent, but in the case of the "basic lead chromates" (*q. v.*) a 50–50 molar % mixture of sodium and potassium nitrates (eutectic at

[1] Chem. Engr. Thesis, Stanford University, 1920; unpublished.

[2] Acknowledgment for this suggestion and many others during the course of the investigation is here made to Profs. R. E. Swain and S. W. Young, of this laboratory.

[3] Schein (with S. W. Young): "The Precipitation of Potassium Sulfate Fumes." Thesis for degree Chemical Engineer, Stanford University, 1920. Unpublished.

218°)[1] was used. This flux was selected because of its low melting point, and because of the marked interaction between sodium chloride flux and lead oxide (*q. v.*).

Procedure.—Components of reaction-mixtures were weighed out in multiples or fractions of mols. It was found advisable to pour the melted flux over the solid reaction-mixture, allow it to stand for a short time, and then gradually stir the whole mass. This procedure was evolved because the fused nitrates do not "wet" solid lead oxide readily; if the latter is added to the melted flux it floats, and is only stirred in with great difficulty, involving considerable loss of time.

Experimental.—Dried lead oxid (PbO) and an excess of anhydrous sodium chromate were mixed with dried sodium chlorid, fused, and the mass kept in a state of quiet fusion for ten minutes, and then poured into water. The characteristic "chrome yellow" resulted, and the reaction was nearly complete.

Anhydrous sodium dichromate is not suited to reactions of this type, the resulting precipitate being badly discolored (greenish brown), and containing compounds of trivalent chromium, as was indicated by the fact that the original yellow color could be restored by fusion (or boiling in water) with sodium peroxid. The presence of trivalent chromium may be accounted for by considering that sodium dichromate dissociates in sodium chlorid fusion, after which the dissociation product chromic anhydrid decomposes into chromium sesquioxid and oxygen, which oxygen oxidizes the PbO to PbO_2 causing further discoloration. Potassium dichromate is also unsuited for these reactions, but is less objectionable than the sodium salt. Ordinarily, both sodium and potassium dichromate dissociate at temperatures well above that of these fusions (about 880°) when either is heated alone, but this dissociation apparently takes place at a much lower tempera-

[1] Landold-Bornstein-Roth: "Physicalische-chemische Tabellen," 4 Auflage, pp. 611–635.

ture in a solution of fused sodium chlorid. Chromic anhydrid decomposes at 250°.[1]

Basic Lead Chromates.—Two such compounds, PbO.Pb-CrO_4[2] and PbO.2PbCrO_4[3] are described in the literature. The former has been prepared by the alkaline hydrolysis (NaOH) of lead chromate, or by fusing the same compound with potassium nitrate, and the latter, together with lead chromate, "by allowing solutions of lead nitrate and potassium chromate to diffuse into one another."[4] Both are described as red compounds. The former was readily prepared as described (see analysis 1, Table II) but it was not found possible to prepare the compound PbO.2PbCrO_4 by the method given. A mixture of one mol lead oxid and two of lead chromate was fused with the nitrate flux, and yielded a scarlet-red mass, which analysis showed to contain:

		Theory for PbO. 2PbCrO_4
PbO	75.08%	76.98%
CrO_3	24.90%	23.02%
	99.98%	100.00%

If a 50–50 molar % mixture of lead oxid and lead chromate were allowed to interact in fused sodium chlorid solution, a substance closely approximating the composition PbO.PbCrO_4 resulted. If the melted fusion were poured into water, the resulting precipitate was of a deep orange color; if allowed to cool slowly, it was red. The equilibrium diagram (*q. v.*) points to the cause of this difference in color as partial dissociation of the "basic lead chromate" at the temperature of the bath. Analyses showed:

[1] Roscoe and Schorlemmer: "Treatise on Chemistry," 5th edition, **2**, p. 1029.

[2] Cox: Jour. Am. Chem. Soc., **28**, 12, 1902; Zeit anorg. Chem., **50**, 232.

[3] Roscoe and Schorlemmer: "Treatise on Chemistry," 5th edition, **2**, pp. 1033–1034.

[4] See note (3).

	I. Poured into water (orange)	II. Slowly cooled (red)	Theory for $PbO.PbCrO_4$
PbO	81.91%	81.26%	81.69%
CrO_3	17.91%	18.67%	18.31%
	99.82%	99.93%	100.00%

A 50–50 molar % mixture of sodium and potassium nitrates was used as the vehicle for subsequent attempts to prepare "basic lead chromates, on account of its relatively low melting point (eutectic at 218°). Beside the red substance $2PbCrO_4.PbO$, three other red substances were prepared in the nitrate flux; they approximated the compositions $PbO.PbCrO_4$, $2PbO.PbCrO_4$ and $3PbO.PbCrO_4$, respectively; whether slowly or rapidly cooled, the red color persisted. Their analyses follow:

TABLE I

	PbO	CrO_3
1. $PbCrO_4$, nitrate flux, 225°–230°, 90 minutes	80.37%	19.60%
1*a*. $PbCrO_4$ + PbO, nitrate flux, same conditions	81.86%	18.14%
Theory for $PbCrO_4.PbO$	81.69%	18.31%
2. $PbCrO_4$ + PbO, nitrate flux, 100 minutes	88.26%	11.74%
Theory for $2PbO.PbCrO_4$	87.00%	13.00%
3. $PbCrO_4$ + PbO, nitrate flux, 200 minutes	90.21%	9.83%
Theory for $3PbO.PbCrO_4$	89.82%	10.08%

Insofar as analysis is concerned, there is little difference between the red substances prepared by (1) alkaline (NaOH) hydrolysis of lead chromate, (2) fusion of lead chromate with nitrate flux, (3) fusion of lead chromate and lead oxid (50–50 molar %) with nitrate flux, (4) fusion of lead chromate and lead oxid (same mixture) with sodium chlorid flux, and the orange substance prepared by fusion of the same mixture of lead chromate and lead oxid in sodium chlorid flux, but poured quickly into cold water. Comparative analyses follow:

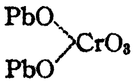
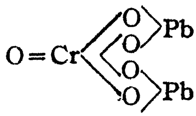
TABLE II

	PbO	CrO_3
I. $PbCrO_4$+10% NaOH, boiled 1 hour (red) .	80.52%	19.41%
II. $PbCrO_4$+nitrate flux, 225°–230°, 30 minutes (red)	80.37%	19.60%
III. $PbCrO_4$ + PbO, nitrate flux, 225°–230°, 10 minutes (red)	81.86%	18.14%
IV. $PbCrO_4$ + PbO, sodium chlorid flux, 10 minutes (880°) slowly cooled (red)	81.26%	18.67%
V. $PbCrO_4$ + PbO, sodium chlorid flux, 10 minutes (880°) quickly poured into cold water (orange)	81.69%	17.91%
VI. Theory for $PbCrO_4.PbO$	81.69%	18.31%

A consideration of the above, and the differences in method of preparation renders the mechanism of reaction and the constitution of the compounds (phase-relations (*q. v.*) clearly indicate the compound $PbCrO_4.PbO$) important questions. That I is an hydrolysis-product can scarcely be doubted; the reaction forming it would, of course, be ionic. The others (II–V) may be products of a reaction similar in mechanism to hydrolysis, but there is nothing to show how the molecules PbO and $PbCrO_4$ are afterward combined. If the reactions are similar in mechanism to hydrolysis, it follows that there will be an interaction between the ions of solvent and solute, hence we must, on this assumption, consider at least this much of the process of formation of basic lead chromates an ionic reaction. There is no reason to believe that the fused nitrates behave any differently from any other flux or solvent (see tests on used flux), hence the general name "solvolysis" for this type of reaction is proposed;[1] it would of course include hydrolysis and ammonolysis. Apparently the color and composition of a given red basic lead chromate prepared as above depend solely upon the time allowed for solvolysis. An inspection of Table I will indicate that the PbO might even be omitted; that the formation of a given red substance depends upon the removal of CrO_3, which would require a longer time without the added PbO.

[1] Suggested by E. C. Franklin.

All this would tend to show that the red substances are produced in two steps: (1) lead chromate solvolyzes; (2) it combines with PbO. This does not carry one very far in the way of an explanation, nor does it decide whether the red substances are constituted:

(1)  (2) $PbO...PbCrO_4$ (3) 

The logical conclusion would be that the substances were either "higher order" compounds (1, 2) or the lead salt of a chromic acid containing four hydroxyl-groups, i. e., an ordinary "valence compound" (3). Such a chromic acid would correspond to what might otherwise be termed a "hydrate" of the ordinary chromic acid, i. e., $H_2CrO_4.H_2O$ (H_4CrO_5). This "hydrate" of chromic acid is strictly analogous to one of those known for sulfuric acid.[1,2] It must also be borne in mind, that beside the two structure-possibilities already mentioned one must include the possibility that these red compounds are true basic salts. Such conception excludes the possibility of other than the ordinary chromic acid, but not the "higher order compounds" already referred to. Again, from the standpoint of the Phase Rule, any composition is possible, depending on temperature, pressure and concentration. None of the explanations offered are satisfactory for a substance of the composition $3PbO.PbCrO_4$ nor are they sufficient to enable the prediction of such a compound. A study of the freezing-point diagram, (*q. v.*) however, does not reveal any such compound; at that composition there is indicated a solution of $PbCrO_4.PbO$ and $PbCrO_4.4PbO$ in each other.

[1] Pickering: Jour. Chem. Soc., **57**, 1339 (1895).

[2] See Stearns and Young: Jour. Am. Chem. Soc., **38**, 10, 1953, footnote 1. These observers arrived at a similar conclusion concerning the salts of "orthosulfuric" acid. The present conclusion as to "orthochromic" acid was reached independently and without knowledge of the work of Stearns and Young. Dr. Stearns called the writer's attention to the same in the course of a conversation some three months later.

The behavior of a 50–50 molar % mixture of lead oxid and lead chromate in fused sodium chlorid solution is also worthy of notice. As has been previously noted, when the fusion containing such a mixture is poured into water, an orange-colored mass results; allowed to cool slowly, it is red. As the compositions of the red and orange substances are very nearly identical (Table II), the difference in color would seem to indicate a partial dissociation at the temperature of the bath (about 880°), that is $Pb_2CrO_5 \rightleftarrows PbO + PbCrO_4$ occurs, and the sudden chilling "fixes" the system in this condition. Hence the orange-colored mass might be looked upon as a mixture of lead oxid and lead chromate, and the red mass as a definite compound, Pb_2CrO_5. The freezing-point diagram verifies the assumption of dissociation at higher temperatures because:

1. The compound $PbCrO_4.PbO$ is clearly defined (C_3) in equilibrium chart.

2. The maximum C_2 in the freezing-pointcurve occurs at 65–35 molar % instead of at 66.7–33.3 molar % as would be expected, and which latter corresponds to the compound $2PbCrO_4.PbO$ already known.[1] The shifting of this maximum can be explained in terms of such a dissociation.

3. Boiling the orange-colored mass with 10% sodium hydroxid solution for 48 hours did *not* produce the red substance, which apparently indicates that the dissociation-product PbO dissolves more readily in 10% NaOH solution than the dissociation-product $PbCrO_4$. Boiling with more concentrated NaOH solution simply dissolves the entire substance.

In attempting to secure experimental evidence of the mechanism of formation of these "basic lead chromates," the following facts were brought out:

1. A random mixture of lead oxid and lead chromate, heated to fusion without flux, and slowly cooled, yielded a red product.

2. A 50–50 molar % mixture of lead oxid and lead chro-

[1] Pogg. Ann., **28**, 162.

mate treated in the same manner yielded a red product containing 81.67% PbO and 18.28% CrO_3.

3. One mol lead oxid and five of sodium chlorid were fused and kept in a state of quiet fusion for two hours. 99.4% PbO was solvolyzed to $PbCl_2$.

4. One mol lead chromate and five of sodium chlorid were treated as in 3. A muddy-brown to orange mass resulted, which analyzed as follows:

Solvolysis residue		Theory for $PbCrO_4$
PbO	70.20%	68.73%
CrO_3	29.80%	31.27%

showing that 8.25% of the original CrO_3 had been removed by solvolysis. The brown mass closely approximates the composition $17PbO.16CrO_3$, to which theory assigns

PbO	70.32%
CrO_3	29.68%

An inspection of the freezing-point diagram reveals no such compound; the ratio 17:16 is so nearly 1:1 (50–50 molar %) that none should be expected.

5. $PbCrO_4$ was treated for an hour with nitrate flux (fusion poured on solid $PbCrO_4$) at 225°–230° without stirring. After solidification, the upper layer was bright yellow in color and the lower a bright red. Samples of the yellow solid dissolved quickly and completely in water at room temperatures, and reacted strongly for $(CrO_4)^{=}$ but not for Pb^{++} as was to be expected from its dissolving without precipitation of $PbCrO_4$. The lower bright red layer contained.

PbO	73.10%
CrO_3	26.80%

showing the removal of 14.3% of the original CrO_3 by solvolysis. This red substance closely approximates the composition $5PbO.4CrO_3$; that is, $4PbCrO_4.PbO$, represented by the point C_1 in the diagram.

6. A similar experiment, though lasting for two hours, was tried, yielding a bright red substance containing

PbO 80.36%
CrO_3 19.51%

showing the removal of 37.6% of the original CrO_3 by solvolysis. This composition approximates $11PbO.6CrO_3$ (i. e., $6PbCrO_4.5PbO$), not shown to exist; it is probably a solution of $PbCrO_4.PbO$ and $2PbCrO_4.PbO$ in each other.[1] (See diagram.)

7. PbO, treated exactly as in (5) and (6), yielded a *perfectly* white upper layer of solidified flux completely and readily soluble in water at room-temperatures, and reacting for neither Pb^+ nor $(NO_2)^-$. The lower layer of lead oxid consisted of a yellow and a red zone and contained 97.0% PbO; the original PbO contained 99.52%. Calculated to Pb_3O_4, this "loss" of PbO would mean very nearly one molar % of that compound formed in the course of fusion, so that apparently the fusion product is $99PbO.Pb_3O_4$. But the assumption of the formation of Pb_3O_4 must include reduction of nitrate to nitrite (for this experiment), and no nitrite was found; hence, another explanation for the red substance must be sought for. PbO exists in two modifications:[2] (1) yellow, orthorhombic, (litharge); (2) red, tetragonal (massicot). The former is stable up to 620° and is completely transformed into the latter at 720°.[3] This explains the reddening of the PbO at the *bottom* of the vessel (local heating, mass not stirred), also the lack of evidence of oxidation of lead and reduction of nitrate, already referred to. This seems a logical explanation in view of the persistent and pronounced arrest in all of the cooling-curves (except pure $PbCrO_4$) at 625° (*q. v.*), indicated by the line HH′ in the diagram, (*q. v.*). The line NN′ may also represent the transformation from the red modification to another form, since NN′ corresponds to 720°.

A consideration of (5) would lead one to expect a "solvolytic" reaction such as: $PbCrO_4 + KNO_3 + NaNO_3 \rightleftarrows Pb(NO_3)_2 +$

[1] Cox: Jour. Am. Chem. Soc., **28**, 12, 1902.
[2] Hintze: Handbuch der Mineralogie, **1**, 1934 (1915).
[3] Ruer: Zeit. anorg. Chem., **50**, 265 (1906).

$NaKCrO_4$, which should be an ionic reaction. If this were the sole process of mechanism, treatment of the yellow solid flux with water should lead to a reversal of the above reaction. But no precipitation of lead chromate results, and the aqueous solution of this yellow flux will precipitate Pb^{++} from its solutions. Since lead nitrate begins to decompose at temperatures above 205°[1] it would appear that the PbO formed as a result of such decomposition interacts with the $PbCrO_4$ already present. A consideration of (7) would show that Pb^{++} is present in the white flux in lower concentration than that sufficient to exceed the solubility-product of PbS ($=4.2 \times 10^{-28}$) (H_2S test used here for Pb^{++}), and hence if we consider the white flux to be thus free from Pb^{++} ($<4.2 \times 10^{-14}$), we can scarcely consider that the second phase of the reaction is an ionic reaction. While the writer is inclined to the belief that all reactions are ionic, the results recorded would seem to indicate that it need not of necessity follow that such must be the case under all conditions.[2]

Freezing-Point Diagram.—In order to definitely settle the true state of affairs in the system lead chromate–lead oxid, the freezing-point diagram was plotted from cooling-curve data obtained from a series of fused mixtures of the two compounds (without flux), the mixtures progressively differing in composition by 5 molar %. The resulting diagram was checked against photomicrographic evidence. With the exception of pure PbO and 55–45 molar % $PbCrO_4$ + PbO, the specimens were much too soft to permit of good polishing. The surfaces of the other specimens "dragged" and "pitted" to a high degree, and photomicrographs were obtained with difficulty. The freezing-point curves and diagram follow:[3]

[1] Van Nostrand's Chemical Annual, 1918, p. 178.

[2] See W. A. Noyes: Jour. Am. Chem. Soc., **42**, 11, 2174 (1920), footnote 2. The writer reached the same conclusion independently some six months prior to the appearance of this article.

[3] Due acknowledgment is here made to Prof. C. F. Tolman, Geology Department, Stanford, for the use of apparatus and for valuable assistance in the preparation of photomicrographs; also to Messrs. L. E. Porter and M. K. Rouse for assistance in preparing the specimens.

The freezing-point curve XY shows four well-defined maxima (C_1, C_2, C_3, C_4) corresponding respectively to the compounds $4PbCrO_4.PbO$, $2PbCrO_4.4PbO$,[1] $PbCrO_4.4PbO$[1] and $PbCrO_4.PbO$. Apparently the first and fourth of this series have not been reported in the literature. While the point C_2 indicates a concentration of 65–35 molar % $PbCrO_4.PbO$, it is believed that the apparent location of this point is somewhat in error, and that it should correspond to the concentration 66.7–33.3 molar %, i. e., to the compound $2PbCrO_4.PbO$, already known. It will also be noted that the slope of the curve C_2E_2 (upper section) is very steep, so that a slight error in reading would displace the point C_2 sufficiently to cause its apparent location as recorded on the diagram. In the event that the location of the point C_2 is correct, its location with respect to the concentration corresponding to the compound $2PbCrO_4.PbO$ could be explained by considering that the dissociation

$$2PbCrO_4.PbO \rightleftarrows PbCrO_4 + PbCrO_4.PbO$$

commences at a temperature below the melting point of the

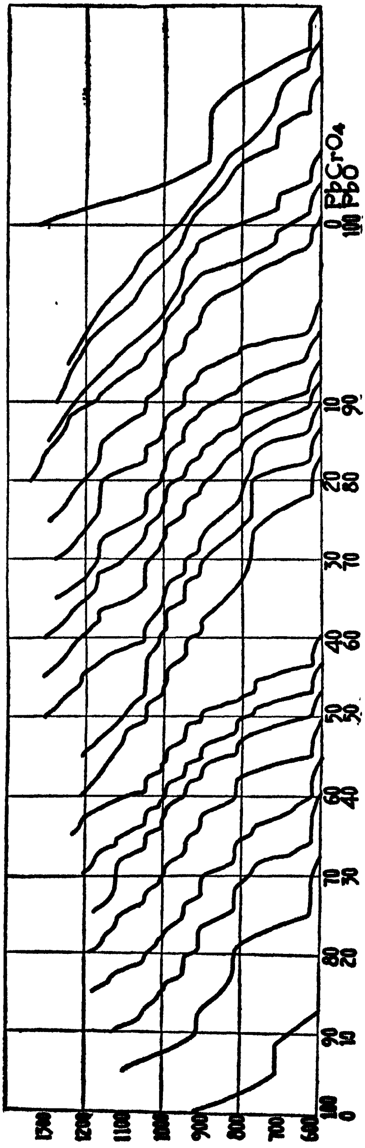


Fig. 1

[1] See notes 2 and 3, p. 547.

compound $2PbCrO_4.PbO$. Photomicrographic evidence apparently confirms this supposition.

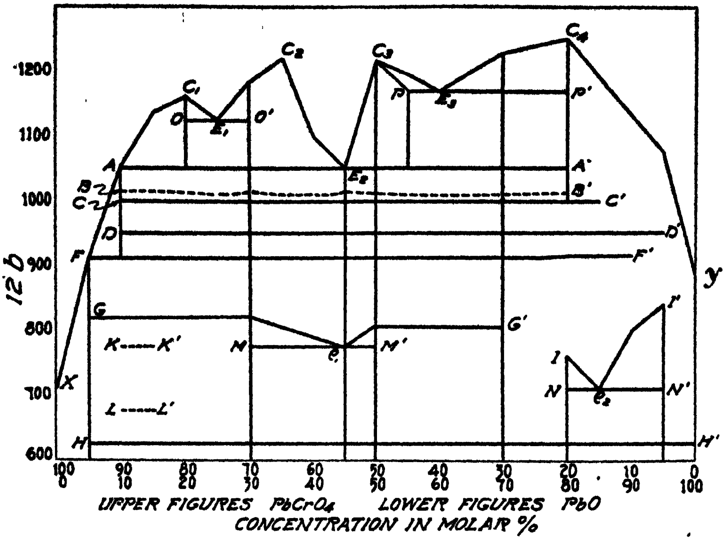


Fig. 2

It is to be noted that the diagram fails to show any other compounds than the four mentioned; this would indicate that the other red substances prepared were solutions of these compounds in each other. It is possible that the slight breaks in those portions of the freezing-point curve marked C_2E_2 and E_3C_4 may be due to the decomposition of other compounds, or perhaps to the influence of the solid eutectics at e_1 in the first case and e_2 in the second. There may be some relation between the break in E_3C_4 and the abrupt ending of the line GG′ at G′. Photomicrographic evidence is lacking in both instances.

The diagram also shows three well-defined eutectics (E_1, E_2, E_3), the influence of the second being noticeable throughout almost the entire system (see AA′) due, perhaps, to the additional influence of the solid eutectic at e_1, both E_2 and e_1 occurring at the same concentration. The influence of the eutectics E_1 and E_3 is indicated by the lines 00′, PP′,

respectively. There are two eutectics (e_1, e_2) in the solid phase, the influence of each being indicated by the lines MM′, NN′, respectively. The line GG′ may indicate that the eutectiferous material is immiscible with the other phases present.

The well defined and very regular lines CC′, DD′ and FF′ (and also GG′) can be interpreted as indicating transitions in the solid phase; this in analogy to the transition between the two crystalline forms of PbO (*q. v.*) indicated by the line HH′. They may also indicate immiscibility in the liquid state at the indicated temperatures.[1] It will be noted that the line GG′ contains the eutectic e_1, and that the eutectics E_2 and e_1 occur at the same concentration, altho observations taken at shorter intervals than 5 molar % might easily indicate a shift of these and other points.

The lines BB′ and CC′ are so close together (10°–15° only) in the diagram that there seems to be a reasonable doubt as to the authenticity of one of them; BB′ is therefore dotted in the diagram. Perhaps a single line at 1010° would approximate the facts better; yet the halts in the cooling curves indicate a slight but definite change at BB′.

The abrupt ending of the lines AA′, BB′, CC′, DD′, FF′ may be explained by considering that the concentration of PbO has reached sufficient magnitude to prevent the settling-out of the phases bounded by these lines at the temperatures and concentrations indicated, i. e., that the phases are now miscible. Observations with mixtures differing by less than 5 molar % concentration might prove of value in fixing the ending of these lines. The abrupt ending of GG′ has already been discussed. The same explanation might be offered for the apparent break between the points G′ and I. One could reasonably expect a continuous line from G to I′, but the cooling curves indicate no points of arrest between the temperatures indicated by the points G′ and I, thus furnishing no

[1] This is known to be true for many alloys. See Hindrichs: Zeit. anorg. Chem., 59, 414 (1908); Lewkonja: Ibid., 293; Desch: "Metallography," 2d edit., appendix, Table III, pp. 402–3.

evidence of the state of the equilibrium under these conditions of temperature and concentration. A possible connection between the abrupt ending of the line GG′ and G′ and the slight break between E_3 and C_4 has already been indicated. A similar explanation might be offered for the fact that there is a break in C_4Y at the same concentration as that indicated by the point I′, altho this break may also be related to the solid eutectic at e_2, as was pointed out for the break in C_2E_2 in connection with the solid eutectic at e_1.

The lines KK′ and LL′ are inserted (provisionally) in the diagram solely for the purpose of making that diagram correspond with the evidence offered by the two cooling curves containing halts at this temperature; repeating the observations with concentrations differing by very small molar percentages might furnish additional evidence. No explanation is offered for these two short lines.

The line HH′ represents the transition from the yellow form of PbO to the red form; this is usually given at 620°,[1] but the observations here recorded repeatedly show 625°. The yellow form of PbO crystallizes in the orthorhombic system[2] (mineral litharge)[3] and the red in the tetragonal[2] (mineral massicot, recently reported).[3] This could be due to slight error in reading or in fixing the calibration-curve for the thermo-couple. It is not a large error —0.8%.

Summary

Reactions in fused salt media can be brought about in such a way as to yield products analogous to those prepared from the same initial reacting substances in aqueous solution. A few typical reactions have been studied.

The chief difference between these reactions and their analogues in aqueous solution lies in the lower velocity of the

[1] Hintze: Handbuch der Mineralogie, **1**, 1934 (1915). Groth: Chemische Crystallographie, **1**, 76 (1906). Geuther: Ann. Chem., **219**, 56 (1883).

[2] Larsen: Am. Mineralogist, **2**, No. 2, p. 8 (1917).

[3] Wherry: Ibid., p. 19.

former, most likely due to the relative insolubility of the reacting substances in the several fluxes experimented with, as compared to water.

In several cases, at least, there is an interaction between the fused salt flux, or solvent, and the solute dissolved therein. So far as the investigation goes, this interaction is analogous to hydrolysis or ammonolysis; the general term "solvolysis" is proposed, intended to include all such interactions.

While the above analogy would indicate that "solvolytic" reactions are ionic in mechanism, the second phase of the reaction forming "basic lead chromates" would point to a reaction not ionic in mechanism. It may be a purely "molecular" (addition) reaction, resulting in the formation of "higher order" compounds. Such a conclusion will satisfactorily explain the slowness of the reactions described, aside from the low solubility of the solutes in the fused salt media.

While at least one basic lead chromate may be prepared by a wet reaction (alkaline hydrolysis) which is admittedly ionic in mechanism, it does not necessarily follow that the basic lead chromates formed in fused salt reaction-media are formed by a wholly analogous process. At least two new "basic chromates" prepared by the latter method have not been prepared in the wet way, and one other, reported as being so prepared, resisted extended attempts to so prepare it. It could be readily prepared by the fusion-method. The existence of the four basic lead chromates is verified by a study of the system lead oxid–lead chromate. Other supposedly basic lead chromates are shown by the same means to be either mixtures or solutions of these compounds in each other.

Lead salts of "orthochromic acid" are shown not to exist. While the salt Pb_2CrO_5 may be a salt of a "monohydrate" of the ordinary chromic acid, it could equally well be a true basic salt or a "higher order" compound, so far as the present investigation is concerned.

At the temperature of the experiments the stable form of PbO is yellow in color. This, combining with yellow lead

chromate, yields red compounds, all of which points to higher order compounds. The red compound formed by alkaline hydrolysis of normal lead chromate could well be considered a basic salt, but the addition of lead oxid and lead chromate molecules to form a higher order compound might as easily take place in aqueous solution as in the nitrate flux used to form a red compound of very closely the same composition.

The reddening of PbO in the nitrate flux has been shown to be due to change in crystalline form, and not to the formation of Pb_3O_4, as might at first be supposed.

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THE SIZE-FREQUENCY DISTRIBUTION OF PARTICLES OF SILVER HALIDE IN PHOTOGRAPHIC EMULSIONS AND ITS RELATION TO SENSITOMETRIC CHARACTERISTICS. II. THE METHODS OF DETERMINING SIZE-FREQUENCY DISTRIBUTION

BY E. P. WIGHTMAN AND S. E. SHEPPARD

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Introduction

In the first paper of this series[1] we discussed the question of a possible relationship between size-frequency distribution of the particles of silver halide in a photographic emulsion and their sensitivity to light action. The most important work in this field which had been done up to that time was considered in detail.

We now turn to the question of the methods for determining size-frequency distribution. For convenience they may be classified as follows:

I. MICROSCOPIC PARTICLES

A. Fractionation by gravity (including the ordinary elutriation method) or by centrifugal force, in which the sizes of the particles in the fractions are estimated:

1. By consideration of sedimentation laws (including Westgren's "wedge" method).

2. By optical control of size determinations by

a. Counting the particles in a haemacytometer cell.

b. Use of the cameral lucida, projection and determination of projective areas by planimetry or other means, or the same method using photomicrography. Method (*b*) may be applied directly to random samples, and in the optical control in general, either transmitted or dark field illumination may be applied.

B. Selective filtration methods.

[1] Jour. Phys. Chem., **25**, 181 (1921); Brit. Jour. Phot., **68**, 169 (1921).

II. Submicroscopic Particles

A. Ultra filtration.

B. Fractional coagulation.

C. Optical grading by counting in fields of varied light intensity and other optical methods.

D. Electrical sedimentation, and other sedimentation methods.

E. Amplitude of Brownian movement, per se, or electric-controlled.

The methods given apply to the determination of frequency curves only, and not directly to the relation of size of grain to sensitiveness. For this we may:

a. Prepare plates from fractions obtained by one of the above methods.

b. Use Svedberg's method[1] of investigation of residual grains in thinly coated very dilute emulsions, "one grain thick."

The present paper will be devoted largely to an account of the size-frequency distribution methods themselves, including a new sedimentation and grain-counting method. The new counting method is only an approximate one, since to make it a fairly rapid means of obtaining the distribution it is necessary to limit the separation of the particles to a comparatively small number of fractions, as explained later. In later papers we shall present the results obtained by the application of more accurate, but also more complicated methods.

We shall pay slight attention in the present paper to the class of submicroscopic particles, although mention of some work which has been done in this field will be made because of its bearing on the subject in general.

Selective filtration methods are rather impractical for the separation of particles larger than ultramicroscopic size and so will be dismissed without further mention.

The basis of most of the experimental work which has been

[1] T. Svedberg: Zeit wiss. Phot., **20**, 36 (1920).

done on size-frequency distribution is sedimentation. It is well known that when a uniform mixture of various-sized particles is allowed to settle, the larger particles sediment with a greater velocity than the smaller, due chiefly to the greater frictional resistance of the liquid medium to the smaller particles per unit of weight, their surface per unit weight being greater.

The work which has been done in the past has been either of purely scientific nature, or has been applied to such questions as the mechanical analysis of soils and other problems not connected with photography.

Incidentally in many of the investigations, Stokes' Law has played an important rôle, and the question as to its validity has had to be considered from several standpoints. We shall give a brief discussion of the law and its limitations, since it also plays no small part in our own experimental work.

Historical

As early as 1899, O. B. Bögghild,[1] by means of Schöne's elutriation method was able to separate four groups of fractions of the following diameters: >0.5 mm; 0.5 to 0.05 mm; 0.05 to 0.02 mm; <0.02 mm, from deep-sea deposits, and measured their number. It is seen that the range of sizes is quite considerable and the limits of the fractions rather extensive.

In 1911, T. Svedberg and K. Estrup[2] made an attempt based upon the principles of Maxwell's distribution law, to determine the relation of the size of particles in a disperse system to their number or weight.

Previous to this J. Perrin,[3] by fractional centrifuging, separated a gamboge suspension containing particles of unequal dispersity, i. e., a heteropsegmatic suspension into homop-

[1] O. B. Bøgghild: Den danske Ingolf-Expedition, Bd i, 3, Havbundens aflagringer af O. B. Bøgghild, S. 18–24 Kjøbenhavn, 1899.

[2] T. Svedberg and K. Estrup: Koll. Zeit., **9**, 259 (1911).

[3] J. Perrin: Comptes rendus, **146**, 967 (1908); **147**, 457 (1908); Ann. Chim. Phys., [8] **18**, 5 (1909); Kolloidchem. Beih., **1**, 254 (1910); Les Atomes, Paris, 1913.

segmatic fractions, or fractions of uniform dispersity. He did not investigate, however, the size-frequency distribution.

Perrin states that if a good separation is desired, the fractionating work, by means of the centrifuge, is a very lengthy process. "In the most careful of my fractionations" said he, "I treated one kilogram of gamboge and obtained after several months a fraction containing a few decigrams of grains having diameters approximately equal to the diameter I wished to obtain."

The size of the grains was determined by Perrin by three different methods:

1. By direct measurement of the radius in the camera lucida.

2. By direct weighing of the grain—first counting the number present in a given volume by a special method.

3. By application of Stokes law.[1]

According to this law the force opposing the steady motion of small spherical particles in a liquid, as deduced by Stokes on purely theoretical grounds is:

$$F = 6 \pi \eta r v \qquad (1)$$

in which

F is the resistance of the liquid
π has its usual significance
η is the coefficient of viscosity of the liquid
r is the radius of the sphere
v is the velocity of the sphere.

From this it follows that if a sphere of density σ moves in a liquid of density σ_1, and is acted on by no external force except gravity, then the sphere will have a uniform velocity when the force of gravity is just equal to the internal resistance, i. e., when

$$F = 6 \pi \eta r v = \frac{4}{3} \pi r^3(\sigma - \sigma_1)g, \qquad (2)$$

[1] G. G. Stokes: Cambr. Phil. Trans., 8, 287 (1845); 9, 8 (1851); Mathematical and Physical Papers, 1, 75, London (1880).

Perrin[1] and others[2] have shown the applicability of this law to colloidal suspensions. Its validity has also been tested for coarse suspensions and for individual particles falling through liquids (and gases) by a large number of investigators.[3]

The equation of Stokes has certain limitations based upon the following assumptions.[4]

1. That the falling particle is a sphere.
2. That the discontinuities of the fluid are small compared with the size of the sphere.
3. That the liquid is infinite in extent.
4. That the sphere is smooth and rigid.
5. That there is no slip at the surface between sphere and fluid.
6. That the velocity of the sphere is small, so small that those terms in the equation of motion of the fluid which represent its inertia are neglected in comparison with those due to its viscosity, that is, when the motion of the particles is at a uniform rate, the terms of higher order can be dropped.

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[1] J. Perrin: Loc. cit.

[2] T. Svedberg: Koll. Zeit., **7,** 1 (1910);
T. Svedberg and K. Inouye: Arkiv. f. Kemi, etc., **4,** Nr. 19 (1911);
J. Duclaux: Comptes rendus, **147,** 131 (1908);
E. F. Burton: Proc. Roy. Soc., **95** A, 480 (1919).

[3] C. Barus: Amer. Jour. Sci., **57,** 122 (1889);
O. G. Jones: Phil. Mag., [5] **37,** 451 (1894);
H. S. Allen: Ibid., [5] **50,** 323 (1900);
A. D. Hall: Jour. Chem. Soc., II., **85,** 959 (1904);
K. Schottner: Beibl , **3,** 60;
R. Ladenberg: Ann Phys., **22,** 287; **23,** 447 (1907);
C. W. Oseen: Arkiv Mathematik, etc., af. K. Svenska Vet. Akad i Stockholm, **6,** Nr. 29 (1910);
Cunningham: Proc. Roy. Soc., **83** A, 357 (1909);
Millikan: Phys. Rev., Apr. (1911);
H. D. Arnold: Phil. Mag., [6] **22,** 755 (1911);
J. Boselli: Comptes rendus, **152,** 133 (1911);
I. Nordlund: Ark. Mat. Astron. Fysik., **9,** Nr. 13 (1913);
C. W. Oseen: Ibid., **9,** 16 (1913);
A. A. Lebedeff: Jour. Russ. Phys. Chem. Soc., **48,** 97 (1916);
A. Westgren: Ann. Phys., [3] **52,** 308 (1917);
S. E. Sheppard: Jour. Ind. Eng. Chem., **9,** 523 (1917).
Note: This bibliography is by no means complete.

[4] See H. S. Allen: Loc. cit.; H. D. Arnold: Loc. cit.; S. E. Sheppard: Loc. cit.

Certain modifications of the Stokes equation have been made relative to some of these assumptions. These will be mentioned later as occasion arises.

Svedberg and Estrup[1] specified two means of ascertaining the frequency distribution of particles in a colloidal disperse system:

1. To determine the velocity of the fall of particles by means of Stokes' law, which may be written in the form

$$r = \frac{9}{2}\sqrt{\frac{\eta}{(\sigma - \sigma_1)g} \cdot V} \tag{3}$$

or

$$v = \frac{2}{9} g r^2 \frac{\sigma - \sigma_1}{\eta} \tag{4}$$

2. To determine the layer changes due to Brownian movement by means of a formula deduced by Einstein[2] and by Smoluchowski[3] and applied by Perrin[4] in the form

$$\frac{F}{v} = 6\,\pi\,\eta\,r = \frac{RT}{N} \cdot \frac{2}{\lambda_x^2}, \tag{5}$$

i. e.,

$$r = \frac{RT}{N} \frac{1}{3\,\pi\,\eta\,\lambda_x^2}, \tag{6}$$

where R and T have their usual significance, N is Avogadro's constant, and λ_x^2 is the mean square of the projection of the displacement of the particle on the horizontal or x-axis.

The method for counting the particles, used originally by Perrin and later by Svedberg and Estrup[5] need not be gone into in detail here, since it has to do with particles of colloidal size, i. e., smaller than those with which we shall deal in the present paper. Suffice it to say that the method was to

[1] T. Svedberg and K. Estrup: Koll. Zeit., **9**, 259 (1911).

[2] A. Einstein: Ann. Phys., [4] **19**, 371 (1906); **22**, 569 (1907).

[3] Smoluchowski: Bull. Acad. Cracovie, Cl. sc. math. et nat., p. 577 (1906); Ann. Phys., [4] **21**, 756 (1906).

[4] J. Perrin: Ann. Chim. Phys., [8] **18**, 5 (1909); Kolloidchem. Beih., **1**, 266 (1909–10); Atoms, p. 113, New York, 1916; Trans. D. Ll. Hammick.

[5] T. Svedberg and K. Estrup: Loc. cit.

determine the distribution by direct observation of the single particles in an ultra-microscope, as many as 200 separate observations being requried. Where velocity of fall is comparatively great, as in coarse suspensions, the method is very difficult if not impossible.

Another method for determining the distribution of the particles of different sizes is that suggested by S. Odén,[1] of fractional coagulation, but it is naturally of very limited application, and also is more suitable for colloidal than for coarser suspensions.

This same author later, however, invented a very neat indirect method for obtaining the distribution curve of the particles settling from a suspension by determining the rate of sedimentation. "The weight of sediment which settles down on a certain bottom area during a unit of time" is measured, and by "plotting this (increasing) weight against time, one obtains a 'precipitation- or accumulation-curve,' from which the distribution-curve may be calculated by a mathematical analysis." This work was the subject of several papers,[2] in the last of which, among other things the size-distribution of a suspension of silver bromide was studied.

We propose to make use of this method later, and so it will be referred to more in detail in a subsequent paper. It may be mentioned here, however, that C. G. Knott[3] has presented in a somewhat simpler form the essence of Odén's mathematical discussion. An advantage claimed for Knott's analysis is that it does not require the use of Stokes' law.

Somewhat earlier than Odén's first work Schloesing[4] had proposed a method for determining the weight—or size-distribution of particles in soils. Both the method itself and

[1] S. Odén: Arkiv. Kemi utg. af. K. Svenska Vet.-Akad, Stockholm, **3**, Nr. 31 (1910); S. Odén and E. Ohlon: Zeit. phys. Chem., **82**, 78 (1913).

[2] S. Odén: Intern, Mitt. und Bodenkunde, **5**, 257 (1915); Proc. Roy. Soc. Edinburgh, **36**, 219 (1915–16); Koll. Zeit., **18**, 33 (1916); Studien über Tone, I.–IV., Bull. Geol. Inst. Upsala (1917–19); Koll. Zeit., **26**, 100 (1920).

[3] C. G. Knott: Proc. Roy. Soc., Edinburgh, **36**, 237 (1915–16).

[4] T. Schloesing père: Comptes rendus, **136**, 1608 (1903); **137**, 369, 398 (1903).

the mathematical treatment of it were very simple. Schloesing allowed about 10 grams of the soil to settle by gravity through water in a vessel so constructed that he could collect directly the fractions of various-sized particles as they settled, so that all he had to do then was to dry and weigh them, and from these weights calculate the amount of each size present.

The mathematical treatment is given in Schloesing's first paper, and here again Stokes' law is not taken into consideration.

Letting $S_1, S_2, \ldots S_n$ represent the weights of the various fractions settling and $D_1, D_2, \ldots D_n$, the sums of the deposits of each fraction in times $t_1, t_2, \ldots$, starting from the same instant, Schloesing deduced the following relation:

$$S_1 = D_1 - D_2 \frac{t_1}{t_2 - t_1}, \; S_2 = D_2 \cdot \frac{t_2}{t_2 - t_1} - D_3 \cdot \frac{t_2}{t_3 - t_2}, \ldots S_n = D_n . \frac{t_n}{t_n - t_n -},$$

and to make it easier for the numerical calculation he assumed the times as powers of 2, so that the above equations (7) reduced to the forms

$$S_1 = D_1 - D_2, \; S_2 = 2D_2 - D_3, \; S_3 = 2D_3 - D_4, \ldots, S_n = 2D_n \quad (8)$$

Schloesing states that in the application of this theory to soils, "it would be useless to collect a great number of successive deposits corresponding to the various fractions (i. e., to all the sizes of grains); suffice it to define the mixtures of sand studied. But it will be understood that any one fraction will be composed not of particles having all the same velocities of fall, but also will include those of intermediary velocities between the two limits set for the fraction."

The limiting sizes of the fractions set by Schloesing are shown in the following table:

TABLE I

Fraction of sand	Limiting diameters of grains in μ
S_1	90–70
S_2	80–65
S_3	70–50
S_4	50–30
S_5	35–20
S_6	20–15
S_7, S_8, S_9	15– 5

They are almost all larger than the largest particles with which we shall have to deal. The extreme limits for all the particles, in our own case, it will be seen later, are from about 8.5μ down to molecular size; but practically, however, from 3 or 4μ to 0.2μ, i. e., a range of sizes just above what is arbitrarily considered the upper limit of size of colloidal particles.

Schloesing showed that the presence of colloidal particles (of the same material) along with the coarser ones had no appreciable effect on the deposition of the latter, even when the colloidal particles constitute as high as 50% of the mixture.

He also found that the rate of fall is independent of the height and that the rate of accumulation is likewise independent of the height. This was later substantiated by Odén.

The apparatus used by Schloesing while very simple, inexpensive, and well adapted to the deposition of soils in which the particles are comparatively coarse, could not be applied to our own work. A further objection to it from our standpoint is that the particles of the substance used in our own work have a very strong tendency to adhere to the surface of the vessel in which they are placed when they come in contact with it, and thus they could not be removed in the manner described by Schloesing.

Another important method of obtaining a distribution curve of the particles is one used by Westgren,[1] based upon Einstein's equilibrium equation[2] for the fall of colloidal particles and upon the work of Perrin on the same subject.[3]

Westgren summarized the method in the following words. "The suspended particles collected in a rectangular microscope chamber are accumulated by sedimentation along a pizeine[4] edge. The preparation with the edge upwards is then placed vertically (180° from the original position). While the particles fall from a horizontal plane, they separate owing to their

[1] A. Westgren: Zeit. anorg. Chem., **94**, 193 (1916).
[2] A. Einstein: Ann. Phys., [4] **19**, 371 (1906); **22**, 569 (1907).
[3] J. Perrin: Comptes rendus, **146**, 967; **147**, 475 (1908).
[4] Optical wax.

varying weights into elements of approximately the same size. By turning the preparation sideways through an angle of 90°, they are sedimented towards the perpendicular straight pizeine edge in the chamber, and with the aid of Einstein's formula for the distribution by weight of the particles in a homogeneous disperse system, knowledge is obtained on the size of the particles occurring in sols, as well as on their relative number."

Since we intend to use this method also later, it will be referred to more in detail at the time.

Hodgson,[1] in 1917, carried out some interesting work on the physical characteristics of the elementary grains of a photographic plate in which he made microscopic measurements of the sizes of particles of halide in various kinds of photographic film. The following table is reproduced from his paper.

TABLE II

Plate	Average grain size*	Range in grain size‡	Shapes
Cine positive film	1.0μ	0.2–2.0μ	Regular, uniform
Seed 23 plate	2.0μ	0.2–3.5μ	Regular, uniform
Seed graflex plate	3.2μ	0.2–6.0μ	Irregular, wide variety
Special experimental emulsion	4.0μ	0.2–8.5μ	Very regular variety

*Greatest dimension
‡Resolved

Here the maximum and minimum sizes are given, and the average size,[2] but no attempt was made to obtain the distribution of the various sizes.

In our previous paper we plotted an approximate frequency curve for the data given by Svedberg[3] for the very dilute emulsion which he prepared. His data upon which the curve is constructed are of course very meagre, so that the curve represents only a very rough estimate of what it should be. For instance, in the case of the smaller sizes, these may

[1] M. B. Hodgson: Jour. Franklin Inst., **184**, 705 (1917); Brit. Jour. Phot., **64**, 654 (1917).

[2] Note: Hodgson does not state how he obtained the average size.

[3] T. Svedberg: Zeit. wiss. Phot., **20**, 36 (1920).

easily differ in number by as much as is shown in Fig. 1 and still give the same mean value for the area.

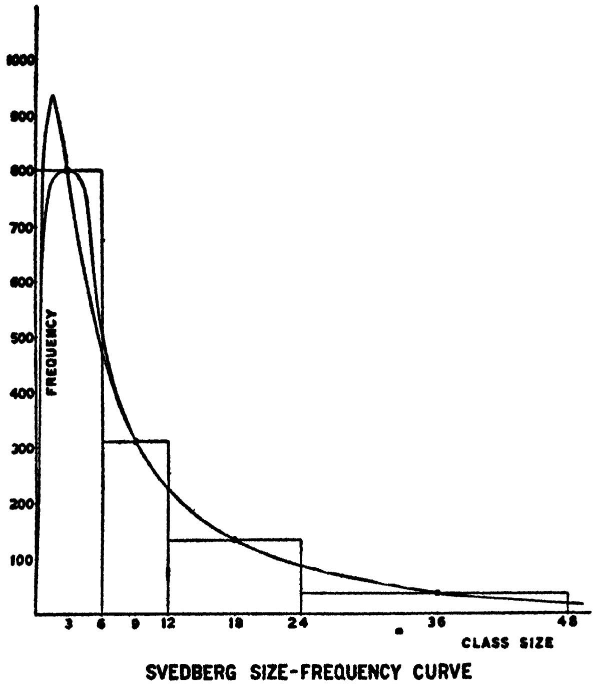

Fig. 1
Size-Frequency Curve from Svedberg's Data

Svedberg's method was fully discussed in our previous paper,[1] and so need not be considered further here.

Other papers on the question of size-frequency distribution to which we have not been able to obtain access are one by Wiegner[2] and another by Pratolongo.[3]

Experimental

Apparatus.—The apparatus used in this work consisted principally of the following:

[1] E. P. Wightman and S. E. Sheppard: Loc. cit.
[2] G. Wiegner: Landwirtsch. Versuchsst, **91,** 41 (1918).
[3] U. Pratolongo: Stazioni sperim. agrar italiani, **50,** 117 (1917).

1. A binocular microscope provided with a Zeiss paraboloid condenser and substage diaphragms, a mechanical revolving stage, and the necessary objectives and oculars—to be mentioned later.

2. An ordinary compound microscope (monocular), provided with Abbe condenser and diaphragms, mechanical stage and objectives and oculars as above, camera lucida, and standard 0.01–0.1 mm ruling for obtaining magnification, as well as an accurate Grayson ruling 8,000 to 60,000 lines per inch.

3. A special table provided with (*a*) a stand for the microscope, with levelling screws and a head rest to relieve the strain of constant bending over it, (*b*) an illuminating system, consisting of a 250 watt concentrated-filament Mazda lamp and lamp hood, condensing lenses and lenses necessary for

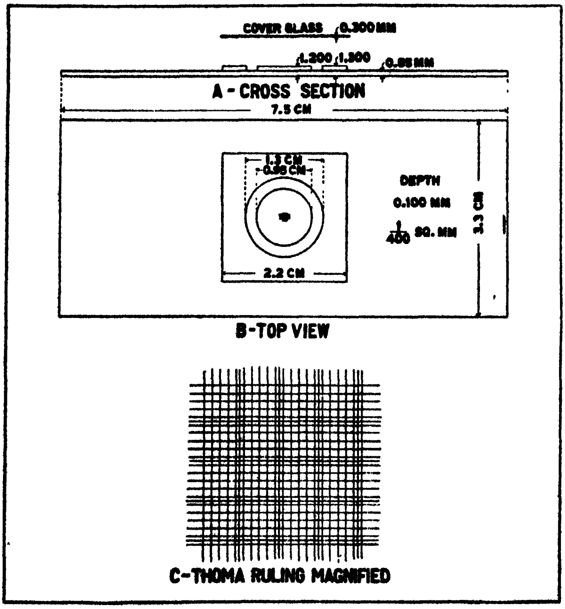

Fig. 2
Counting Chamber
(A) Longitudinal Cross Section
(B) Top View
(C) Thoma Ruling Magnified.

procuring a beam of approximately parallel light, and a water cell for absorbing the heat rays; (*c*) two Veeder counters; (*d*) a black hood over the table to cut off extraneous light.

4. A counting chamber of the Bausch and Lomb type[1] with Thoma ruling. The chamber was specially made to be used for dark field illumination work with a Zeiss paraboloid condenser, and was much thinner than the ordinary type. The dimensions are given in Fig. 2.

5. A constant speed centrifuge with rheostats for adjusting to speeds desired, and a mileage speedometer directly attached and calibrated to read in revolutions per minute.

6. A polar planimeter for determining projected areas.

7. Sedimentation tubes, pipettes and other measuring apparatus, and general laboratory appliances.

Preliminary Procedure

The initial suspensions employed in the following experiments consisted of silver halide particles from a photographic dry plate, or from the original gelatine emulsion from which such plates are made, dispersed in a given volume of 25% glycerine in water.

In the preliminary experiments pure water was used as the dispersion medium but it was found that the larger particles sedimented too rapidly in this.

It is seen from the following table (Table III), which gives

TABLE III

Mean Values of Viscosity and Density of Glycerol, Water, and Mixtures of the Two

Medium	Wt. of glyc. in 100 g. water	η 25°	Temp. coeff. ϕ 25°–35°	Temp. coeff. ϕ 35°–45°	$d\left(\frac{25°}{25°}\right)$
Glycerol	∞	5.862	.124	.101	1.259
75% Glycerol	300	0.3170	.0664	.567	1.192
50% Glycerol	100	0.06112	.0433	.0380	1.127
25% Glycerol	33.3	0.01996	.0323	.0268	1.061
Water	0	0.00891	.0237	.02045	1.000

[1] This was later replaced with a Levy chamber with Thoma ruling.

the mean values of viscosity, η, and density, d, of glycerol, water, and mixtures of the two at 25°, calculated from the work of Jones and coworkers,[1] that 25% glycerin-water has about twice the viscosity of pure water, and hence, according to Stokes' law (Equation 4 above) the velocity of sedimentation should be about one-half as great in this medium.

A 50 cc sample of the suspension, to be described, was centrifuged at about 1600 to 1800 r. p. m. for half an hour and the viscosity of the supernatant liquid, which was practically free of the disperse phase, was determined at 25°. It was found to be $\eta = 0.0195$ which is in fairly close agreement with the value given in the preceding table.

The exact procedure followed in making up the initial suspension was as follows:

1. A 4 x 5 inch (129 sq cm) dry plate was immersed in 40 cc of pure water at 40° in a porcelain-lined developing tray which had just previously been thoroughly steamed,[2] and the whole was placed in an oven at 40° for about four or five minutes. It was then taken out and agitated to remove as much as possible of the silver halide-gelatine emulsion and the suspension was poured into a 200 cc measuring flask.

2, 3, and 4. The plate was bathed and washed three times successively with 25 cc of water at 40°, and the washings were poured into the same flask, a camel's hair brush was used to assist in the removal of the more strongly adhering particles.

5. 75 cc of a glycerine solution containing 53.29 g of glycerine (sufficient to make a 25 % solution by weight) was added to the flask.

[1] H. C. Jones: Monographs Carnegie Inst. Wash., No. 180

[2] It was found that the halide particles—with a thin coating of gelatine over them most likely—had a tendency to stick to the walls of the vessels in which they were placed, i. e., if these vessels were merely cleaned in the ordinary way and washed with cold distilled water. Steaming them immediately before use, however, eliminated this difficulty to a large extent, at least, for a time sufficient to obtain the desired results. All glass apparatus except the counting chamber was therefore treated in this way. The latter required a special treatment which will be mentioned later.

6. Finally, the solution in the flask was diluted to 200 cc at 25°. After thorough agitation this suspension was then ready to be used for sedimentation experiments.[1]

This procedure which was used as said above, in making the initial suspensions for the sedimentation experiments, is, of course, subject to modification. The quantities here given were found to be those most suitable for the apparatus we were using and for obtaining the desired concentration of suspended halide particles.

It is proposed shortly to check up this sedimentation method against the photomicrographic or camera lucida method (described below). For the latter the suspensions are not made up in 25% glycerine solution but in 2% gelatine or some other medium which will allow the suspension when placed in a thin layer on a microscopic slide, to dry completely and evenly, i. e., with uniform distribution.

Now let us turn aside for a moment from an account of the procedure and consider the question of the sedimentation of the silver halide particles which are not at all uniform in shape.[2] It is known that the particles are crystalline[3] and it has been established in this laboratory that they are all modifications of the octohedral classes of the regular system.[4] The majority of the crystals are flat tablets, though there are also many thick and truncated forms, and some fragmentary crystals.

Let us assume that these irregular grains in their fall obey Stokes' law, which as a matter of fact, we have reason to believe (from some preliminary experiments which we have performed) that they do, as we shall see later.

Let us further assume that the specific gravity of the parti-

[1] Experiments are in progress to determine how drastic the means employed to remove gelatine from the silver halide particles may be without affecting them.

[2] M. B. Hodgson: Loc. cit.

[3] E. Banks, Phot. Jour., 22, 159 (1898); M. B. Hodgson, loc. cit; F. W. T. Krohn, Phot. Jour., 58, 193 (1918).

[4] A. P. H. Trivelli and S. E. Sheppard: The Silver Bromide Grain, Monograph No. 1, Eastman Research Laboratory, April, 1921.

cles is that of ordinary silver bromide, 6.473; the sp. gr. of the dispersion medium to be the same as for 25% glycerine solution at 25°, 1.061 (from Table III above); and that the viscosity is also the same as for 25% glycerine (see Table III); further let all these factors remain constant. We have then, from Equation 4:

$$v = \frac{2}{9} g r^2 \frac{\sigma - \sigma_1}{\eta} = Kr^2$$

$$= \frac{2}{9} .980 . \frac{6.473 - 1.061}{.01996} . r^2 = 59050\, r^2$$

From this velocity and the height of the liquid through which sedimentation takes place, can be calculated the total time of sedimentation of any particle of given radius[1] ranging from 0.1 to 4.25μ.

TABLE IV

Times of Settling by Gravity, According to Stokes' Law

r in μ	r^2 in cm^2	v in cm per min. $= K \times 60 \times r^2$ $= 4.0 r^2 \times 10^6$	7.4*/v in min.	7.4*/v in hrs.
4.25	1.81×10^{-7}	0.640	11.7	—
4.00	1.60×10^{-7}	0.567	13.0	—
3.50	1.23×10^{-7}	0.434	17.0	—
3.00	9.00×10^{-8}	0.319	23.2	—
2.50	6.25×10^{-8}	0.220	33.5	—
2.00	4.00×10^{-8}	0.142	52.0	.87
1.75	3.06×10^{-8}	0.108	69.0	1.15
1.50	2.25×10^{-8}	0.080	92.5	1.54
1.25	1.56×10^{-8}	0.055	135	2.25
1.00	1.00×10^{-8}	0.0354	209	3.5
0.75	5.62×10^{-9}	0.0209	354	5.9
0.50	2.50×10^{-9}	0.0089	831	13.8
0.25	6.25×10^{-10}	0.00221	55.8 hrs.	2.3 days
0.20	4.00×10^{-10}	0.00142	86.7	3.6
0.15	2.25×10^{-10}	0.00080	154	6.4
0.10	1.00×10^{-10}	0.000354	348	14.5

*This is the depth of the liquid in the tube in the experiments given below.

[1] S. Odén: Koll. Zeit., **18**, 33 (1916).

Some preliminary sedimentation experiments on the question of the rate of fall of the particles seem to show that they obey Stokes' law. More work is being done on this and details will be given later.

If the particles actually do obey Stokes' law it is rather surprising in view of the fact that the majority of them have the flat tabular form.[1] Such a result might be ascribed to rotational and other Brownian movement which the particles have. The tendency to slip and coast in a zigzag fashion down through the suspending medium is prevented by rotation and irregular motion in all directions. Perrin[2] has shown that microscopic spherules suspended in a liquid obey Stokes' law in spite of the Brownian movement. The halide particles probably behave, therefore, as if they were spheres with a Brownian movement. The effective diameter would be that of a sphere equal in volume to the mean figure of revolution of the particle. It is what Odén and others call the equivalent diameter.[3]

On account of the long time necessary to sediment the finer particles, centrifugal force was made use of in place of gravity. Now the force acting on a particle in the centrifuge is $\frac{4\pi^2 n^2 r}{g}$ times that of gravity. Multiplying Equation 4 above by this factor we get

$$V_c = \frac{2}{9} gr^2 \frac{\sigma - \sigma_1}{\eta} \cdot \frac{4\pi^2 n^2 r_c}{g}$$

$$= \frac{2}{9}\frac{\sigma - \sigma_1}{\eta} 4\pi^2 r^2 n^2 r_c = Kcr^2 n^2 r_c \qquad (10)$$

---

[1] For consideration of the fall of irregular shaped particles in a liquid see:

A. D. Hall: Jour Chem. Soc., **85** II, 959 (1904).
R. Gans: Münchener Ber., **191** (1911).
J. Boselli: Comptes rendus, **152,** 133 (1911).
K. Prizibram: Sitzungsber. Akad. Wiss., Wien, **121,** IIa (1912).
A. Atterberg: Intern. Mitt. Bodenkunde, **2,** 319 (1912).
S. Odén: Koll. Zeit., **18,** 33 (1916), etc., Loc. cit.

[2] J. Perrin: Comptes rendus, **146,** 967; **147,** 475 (1908).

[3] S. Odén: Loc. cit.

in which n represents the number of revolutions per second and r_c the radius of centrifugal action, i. e., the distance from the axis of rotation to the particle at any instant. To obtain the mean velocity we use $r_c = \frac{r_1 + r_2}{2}$, where r_1 and r_2 are the radii to each end of the tube.

In the centrifuge the radius r_2, i. e., the maximum radius was 13.4 cm, and r_1, the minimum radius was 6 cm, hence the mean radius was 9.7 cm. From (10) then we get, using the same value for σ, σ_1 and η as above,

$$V_c = \frac{2}{9} \cdot \frac{6.473 - 1.061}{.01996} \cdot 4 \times 9.87 \times 9.7 \times r^2 n^2$$
$$= 23024\, r^2\, n^2 \qquad (11)$$

If we set 5 r. p. s. (i. e., 300 r. p. m.) as the lowest speed of centrifuging then (11) becomes

$$V_c = 5.756 r^2 \times 10^6 \qquad (12)$$

Table V gives the rates and times of settling of different size particles for various centrifugal rates.

TABLE V

Times of Settling by Centrifugal Force, According to Equation (11)

r in μ	r^2 in cm^2	r. p. m.	r. p. s. = n	n^2	V_c in cm/min. $= K_c \times 60 r^2 n^2$	t in min. for 7.4 cm
1.50	2.25×10^{-8}	300	5	25	.778	9.5
1.00	1.00×10^{-8}	450	7.5	56.3	.778	9.5
.75	5.62×10^{-9}	600	10	100	.778	9.5
.50	2.50×10^{-9}	900	15	225	.778	9.5
.375	1.41×10^{-9}	1200	20	400	.778	9.5
.25	6.25×10^{-10}	1800	30	900	.778	9.5
.20	4.00×10^{-10}	1800	30	900	.497	14.9
.10	1.00×10^{-10}	1800	30	900	.124	59.5

It might be well to mention at this point that various investigators have shown that there is a limiting size of the particle above which it does not obey Stokes' law. The radius of the particle of this size is called by some authors the "critical radius," $\bar{r}$. It naturally differs according to

the density of the particle and the medium, and to the viscosity of the medium. Allen[1] has given the following equation from which it may be calculated, and which he has verified experimentally.

$$\bar{r}^3 = \frac{9\eta^2}{2g\,\sigma_1\,(\sigma - \sigma_1)}$$

In order to determine how the radius of the particles with which we are concerned compared with this critical radius, we calculated $\bar{r}^3$ for a sphere of silver bromide under the conditions of our experiments and arrived at the value

$$\bar{r} = 0.00189 \text{ cm}$$

which is about 10 times greater than the equivalent radius of our largest particles.

Allen's value for a sand particle falling in water at 15° is 0.0085 cm, i. e., about four and a half times larger than for silver bromide in 25% glycerine at 25°. This is about what would be expected from the greater density of the halide and the higher viscosity of the suspension medium.

As to the diameter of the cylinder through which the particles fall having an influence, it is not likely there was any appreciable effect in our experiments, since the ratio of the diameter of the particle to that of the sedimentation vessel was about 1 to 20,000.[2]

Only a few settling periods were chosen for the preliminary work. The periods for settling by gravity were 15 min., 30 min., 1 hr., and 3 hrs. Obviously, time is thus gained at the expense of accuracy, i. e., of a well-defined sedimentation curve. However, for trial purposes these are quite sufficient.

A water-driven centrifuge was first employed for settling centrifugal force, but it was soon found that the pressure by varied considerably and thus prevented obtaining concordant results. The voltage on an ordinary electric line was also too variable to get anywhere near constant speed even for

[1] H. S. Allen: Phil. Mag., [5] 50, 323 (1900).

[2] See S. E. Sheppard: Jour. Ind. Eng. Chem., 9, 523 (1917).

as short a period as ten minutes and was even worse from one period to another.

However, this difficulty was overcome by using a constant speed regulator of the Leeds and Northrup type attached to the motor.[1] The use of an expensive tachometer was avoided by attaching directly to the shaft of the centrifuge, by a universal joint, an ordinary mileage speedometer which was then calibrated to read r. p. m. Certain delays in getting this apparatus set up, and in moving to a new laboratory have prevented more than just a few tests being made on this part of the method. Nevertheless, it was thought worth while to include a description of it in this paper.

The method of procedure in obtaining the counts of the particles in the various fractions was as follows. After settling or centrifuging for the given length of time the supernatant liquid was poured off as completely as possible and the resulting residue was made up to a given volume with distilled water, care being taken that the particles were completely and uniformly distributed before taking the sample for counting.

Reproducibility of results was the first aim. So an experimental technique had to be evolved for this purpose. A number of questions had to be considered and will be taken up in the order investigated.

1. *The Method of Counting.*—The counting chamber is shown in Fig. 2 (page 572). To obtain reproducible counts (mean number of particles per small square) it was found necessary to count both diagonals of large squares, but not all of the squares. One diagonal, however, did not prove to be sufficient.

Owing to the large amount of Brownian movement exhibited by the particle discrepancies in the count arose, but errors were largely eliminated by repeating the count two or three times and taking the average.

2. *The Magnification.*—Since the particles were all sizes from 4μ diameter to molecular size, it was not possible to

[1] This regulator has been described elsewhere by P. G. Nutting: Phot. Jour., **40,** 172 (1916).

reveal all of them no matter what magnification and method of illumination were used. Trials were made with various objectives and eyepieces to determine which were most suitable.

It was found that for general use the Bausch & Lomb 8 min. objective and 12.5 × eye-piece, together with a paraboloid condenser to give dark field illumination gave very satisfactory results, and that with these, all the particles within the range of 4μ to 0.2μ could be seen and counted, the magnification being 260×. This magnification would be too small for use with transmitted light.

3. *Consecutive Counts from the Same Suspension.*—At first no agreement whatever could be obtained between two successive counts on separate samples of the same suspension. This was attributed to three possible sources of error. (1) Either the technique of filling the counting chamber was at fault, (2) the chamber itself was not properly cleaned after each operation, or (3) there was a possible change in the suspension during the interval in which the count was made. The first two were both found to have caused the trouble.

After several trials of various methods for filling the counting chamber, from a blood-counting pipette; by a drop from the end of a stirring rod; etc.; the method finally adopted was to transfer a small drop of the suspension to the chamber by means of an ordinary full pipette with about a 0.4 mm bore at the exit of the lower stem.

A microscopic examination of the counting chamber filled with distilled water after it had first been used with the suspensions and then washed with distilled water, showed that a large number of particles remained sticking to the glass, even though the surface of the ruled disk was swabbed well with a camel's hair brush during the washing.

The scheme finally adopted for removing these attached particles after each count was to place a drop of concentrated ammonia solution on the ruled disk and on the cover glass and to allow them to soak for a few minutes. Then by swabbing the ammonia solution over the surface with the brush and

rinsing thoroughly with distilled water, all the particles of the halide were removed.

The ammonia itself had to be examined from time to time to see that none of the fine glassy spicules, which frequently form in ammonia when standing in glass bottles, were not present, because these spicules also adhere very tenaciously to the surface of the counting chamber and are very difficult to remove by any means.

4. *Counts from Duplicate Sediments.*—It is, of course, important to know whether or not counts made from two separate sediments from the original suspension, treated in the same manner as to time of settling and volume for dilution, would agree. It was found that the results could be duplicated to within 1–4 percent, even when the sedimentation period was only fifteen minutes.

5. *Counts from Two Plates Made from the Same Emulsion.*—It would be expected that two plates when made from the same emulsion, if treated and dried under uniform conditions would have the same number of particles for a given weight of the dried emulsion and that the distribution of the particles according to sizes would likewise be the same. This was also found to be the case within 5 or 6 percent.

6. *The Dilution Necessary for Counting.*—As simple as this problem would seem to be, certain questions are not yet solved.

Each sediment resulting from settling the original suspension for given lengths of time was made up to a certain volume with water, this volume or "dilution" being greater the longer the settling.

The initial dilutions used were as follows:

The sediment from 100 cc of the original suspension were made up to

50 cc	for	the	15 min.	deposition
100 cc	"	"	30 "	"
100 cc	"	"	1 hr.	"
250 cc	"	"	2 "	"

By accident, one of the residues from a 1 hr. deposition was made up to 250 cc while the duplicate was diluted in the

ordinary way to 100 cc. The counts on each when calculated back to the same concentration should have been the same or very close to one another. But they were not. The former was much higher than the latter.

A series of sediments from equal periods of settling were made up to increasing volumes and counts were made on each. The results are given in Table VI.

TABLE VI

No. of sediment	Volume to which diluted	No of particles per sq cm plate (mean value)
1	25	3.92×10^7
2	50	3.14×10^7
3	75	3.45×10^7
4	100	3.82×10^7
5	150	3.89×10^7
6	200	4.93×10^7
7	250	5.62×10^7
8	500	7.63×10^7

It is seen from this table that above a certain dilution—150 cc in this case—the number of particles increases markedly. There are several possible explanations of this, (1) that there is a clumping of the particles in the lower dilutions, and these break up on further dilution; (2) that the individual crystals disintegrate into smaller particles; (3) that the exceedingly fine grains, invisible in the more concentrated suspensions, clumped together and became visible in the greater dilutions; (4) the counting was made by dark field illumination, it is possible that at the high dilutions submicroscopic gelatine particles detached from the grains and were also counted. The last possibility will be checked up by comparing counts by transmission and dark field illumination.

As to the first of these, samples of the more concentrated suspensions were mounted on microscopic slides and examined under high power magnification. The precentage of clumping was found to be less than 1 percent, which would, of course, not be sufficient to explain the increase of 25 to 100 percent in the count.

Data have not yet been obtained in regard to the other possibilities but work on them is in progress. Suffice it to say at this point that the above data give us at least the limit to which the dilution can be carried in order to obtain results, such that clumping is not taking place to an appreciable extent.

In Tables VII and VIII are given the summarized data from a series of sedimentations of the emulsion of two 4 x 5 inch photographic plates, with different emulsions, removed and treated as above described.

No attempt is made here to calculate the size frequency from these data since they are too meagre. Work is now being done on a more complete series of sedimentations with settling periods of $^1/_4$, $^1/_2$, 1, $1^1/_2$, 2 and 3 hrs. by gravity, and three additional periods by centrifuge.

The method of determining the size frequency curves from these data have not yet been worked out, but probably the Odén or the Knott method or a modification of them can be employed.

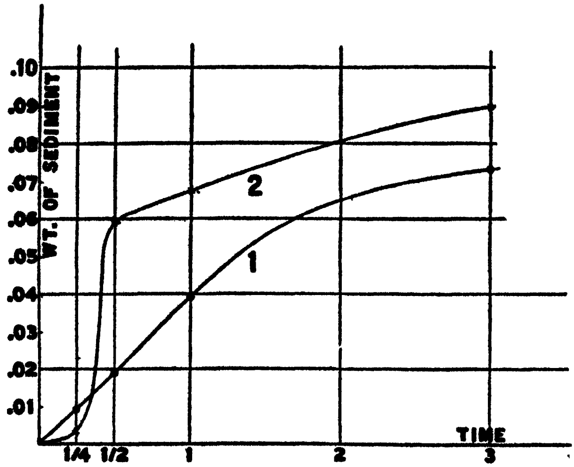

Fig. 3
Weight-Sedimentation Curve

TABLE VII

Plate 1	I 1/4 hr.	II 1/2 hr.	III 1 hr.	IV 3 hrs.	Total from original suspension
No. particles per sq cm plate	1.63×10^7	2.40×10^7	4.98×10^7	9.84×10^7	8.77×10^8
Wt. in g (sedimented portion)	0.0000698	0.000147	0.000302	0.000566	0.001217
Halide per sq cm plate					
Total halides deposited	0.0090	0.0190	0.0730	0.0730	0.1570
Wt. emuls. on 129 sq cm plate					0.4466
Wt. emuls. per sq cm plate					0.003462

TABLE VIII

Plate 2	I 1/4 hr.	II 1/2 hr.	III 1 hr.	IV 3 hr.	Total from original suspension
No particles per sq cm plate	1.48×10^7	2.02×10^7	2.81×10^7	7.05×10^7	
Wt. in g (sedimented portions)	0.0000205	0.000461	0.000523	0.000694	0.001547
Halide per sq cm plate					0.1995
Total halides deposited	0.00265	0.0595	0.0675	0.0895	
Wt. emuls. on 129 sq cm plate	0.00265				0.4744
Wt. emuls. per sq cm plate					0.003678

The sedimentation curves plotted from these tables are shown in Figs. 3 and 4.

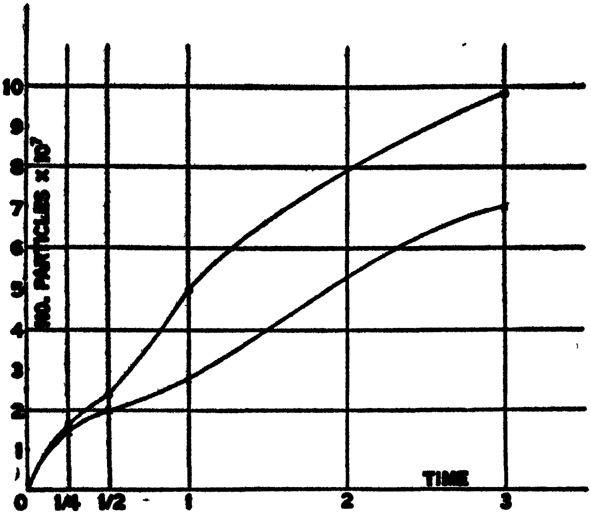

Fig. 4

Frequency-Curve Sedimentation

Determination of Frequency Curve by Counting Grains in Random Sample and Planimetry of Projected Areas

This method, already mentioned—method I A2 (*b*) p. 561 is the most direct, but involves much tedious work in the classification and planimetry of the projected areas. It has been used by us for the mechanical analysis of emery and synthetic abrasives, and is applicable to silver halide emulsions where the grains are chiefly small tabular crystals. A sample is prepared by securing a layer of grains, of 1 grain thickness, uniformly distributed, by allowing a drop of the suspension in 2 percent gelatine, to dry at about 50° on a microscopic slide and then mounting a cover glass on it with Canada balsam, the result of procedure being similar to that of Svedberg. This is magnified as highly as possible, consistent with resolving limits, and the outline copied either with a camera lucida or by photomicrography. The present results were obtained by the former, and were found to agree well with those obtained using photomicrography by Mr. A. P. H. Trivelli, who developed the method at the same time. The first

magnified images are then further enlarged by projection sufficiently for planimetric determination of the individual grains. It is necessary to deal with about 1000 grains to obtain data sufficiently accurate to establish the form of the frequency curve; for emulsions with a very wide range of sizes, such as the one now to be described, even this number is hardly sufficient.

The system used was:

Objective............	Bausch & Lomb 1.9 mm oil
Eyepiece.............	" " " 12.5×
Tube-length..........	208 mm.
Magnification........	ca 3000 diameters
Resolution limit.....	0.3μ

The "fields" obtained (see Fig. 5) were then further magnified, either by an opaque projector, or photographically, some 5 times (see Fig. 6), and the areas of the magnified images

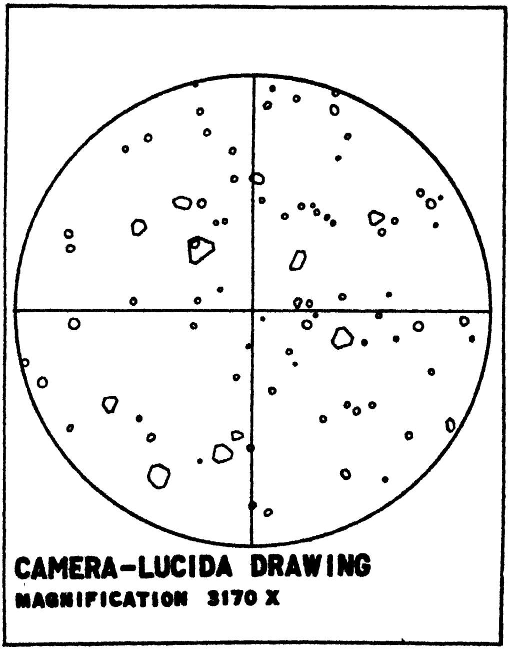

Fig. 5

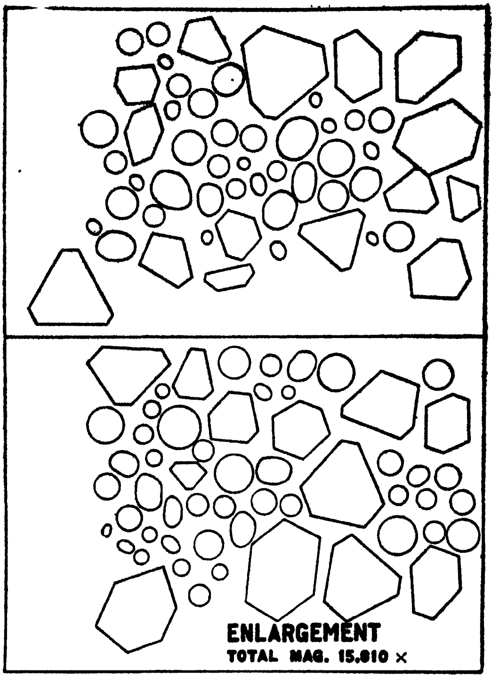

Fig. 6

determined by a planimeter. The planimetric readings were then reduced to actual areas, from the known magnification factors, and the grain-areas ordered in classes and reduced to values per 1000. Graphs were then constructed, plotting frequencies as ordinates, mean (class) projective areas as abscissae. Table IX gives data used to construct Figs. 7, 8 and 9, the mean values for these having been used.

In constructing the curves in the region of the larger grains, where relatively few observations were made, preliminary graphs were drawn, plotting frequency against logarithm of class areas (Fig. 7 and 8), and values from these "smoothed" curves (Fig 8) were used to plot the total frequency curve (Fig. 9). The data obtained for several runs on the same emulsion, show that the reproducibility of the results is quite

as good as could be expected. Sensitometric data on this and other emulsions were obtained at the same time, and the correlation of these with the frequency curves will be taken up in a later paper.

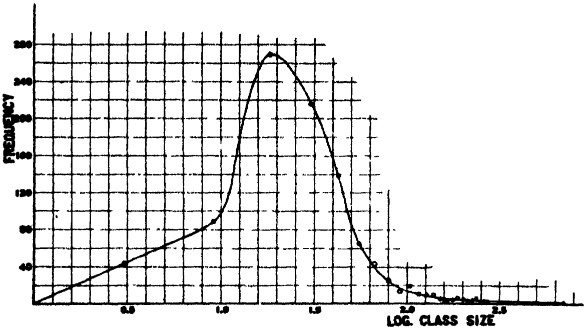

Fig. 7

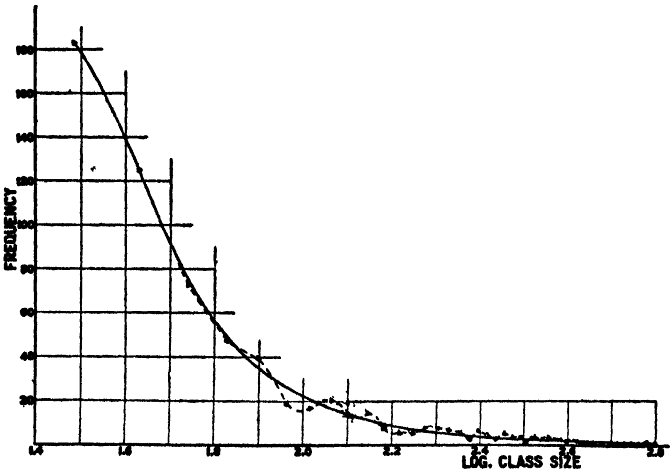

Fig. 8

TABLE IX
Size-Frequency Data

Class no.	Mean class size mm² $\times 10^{-8}$	Log class size	Mean equiv. diam. in μ	No. particles per 1000 original values sample no. 1	2	3	No. particles per 1000 extrapolated values sample no. 1	2	3	Mean	Total area values class size $\times$ no. per 1000 sample no. 1	2	3	Mean
1	3.1	.484	.20	35.5	55.7	57.3	35.5	55.7	57.3	49.5	108	170	175	151
2	9.1	.961	.34	85.6	92.1	75.5	85.6	92.1	75.5	84.4	782	842	690	771
3	18.3	1.262	.48	219.0	201.8	219.6	219.0	201.8	219.6	213.5	4008	3693	4019	3907
4	30.5	1.484	.62	206.8	183.1	177.1	206.8	183.1	177.1	189.0	6307	5585	5400	5764
5	42.7	1.630	.74	120.0	125.1	113.7	124.0	125.1	114.5	121.2	5293	5341	4890	5175
6	54.9	1.740		78.1	72.5	73.6	72.3	75.1	72.5	73.3	3957	4122	3958	4012
7	67.1	1.827		45.0	47.8	46.8	45.0	49.3	47.0	47.1	3020	3309	3154	3161
8	79.3	1.899		29.6	39.5	35.1	30.6	34.9	34.1	33.2	2427	2767	2704	2633
9	91.4	1.961		23.3	18.9	25.8	22.8	26.1	26.9	25.3	2084	2386	2460	2310
10	103.7	2.016	1.15	15.7	17.1	25.5	17.5	20.6	21.9	20.0	1815	2136	2271	2074
11	116	2.064		17.1	20.1	22.6	14.1	16.5	17.9	16.2	1636	1915	2077	1876
12	128	2.107		11.6	12.9	13.1	12.0	13.4	14.8	13.4	1536	1715	1895	1715
13	140	2.146		14.5	14.4	16.5	10.6	11.1	12.2	11.3	1484	1554	1709	1582
14	152	2.182		8.7	7.1	7.3	9.2	9.3	10.3	9.6	1398	1413	1566	1459
15	165	2.217	1.45	10.1	5.6	11.5	8.1	8.0	8.8	8.3	1336	1320	1452	1369
16	177	2.248		7.2	5.0	6.7	7.1	6.9	7.7	7.2	1256	1221	1363	1280
17	189	2.276		3.5	7.7	7.3	6.6	6.0	6.7	6.4	1247	1134	1266	1216
18	201	2.303		3.8	7.7	6.3	5.9	5.2	5.9	5.7	1186	1045	1186	1139
19	213	2.328		5.0	6.5	6.3	5.3	4.8	5.2	5.1	1128	1022	1107	1086
20	226	2.354	1.70	6.3	5.6	4.8	4.9	4.1	4.6	4.5	1107	927	1039	1024
21	238	2.377		4.4	2.1	5.4	4.4	3.7	4.1	4.1	1047	881	976	968
22	250	2.398		3.8	6.2	4.8	4.0	3.2	3.7	3.6	1000	800	925	908

23	262	2.418		5.0	4.1	6.7	3.8	3.0	3.4	3.4	996	786	891	891
24	274	2.438		6.9	2.4	4.5	3.6	2.8	3.2	3.2	987	767	877	877
25	287	2.458	1.91	3.8	5.0	2.2	3.2	2.5	3.10	2.9	919	718	890	842
26	299	2.476		4.4	3.2	2.2	3.1	2.25	2.99	2.78	927	673	894	831
27	311	2.493		1.9	3.5	5.7	2.9	2.15	2.89	2.65	902	669	899	823
28	323	2.509		1.9	1.2	4.1	2.7	2.08	2.78	2.52	873	672	898	814
29	335	2.525		3.8	3.5	2.2	2.6	2.01	2.68	2.43	871	673	898	814
30	348	2.542	2.10	2.5	2.9	2.5	2.3	1.94	2.57	2.27	801	675	895	790
31	360	2.556		1.3	3.5		2.1	1.87	2.47	2.15	756	673	889	773
32	372	2.570		3.1	2.4		2.0	1.80	2.36	2.05	744	670	878	764
33	384	2.584		1.9	2.4	0.6	1.9	1.74	2.26	1.97	730	669	868	756
34	396	2.598		2.5	1.2	1.3	1.75	1.67	2.15	1.86	693	662	852	736
35	409	2.612	2.28		2.1	1.3	1.60	1.60	2.05	1.75	655	655	839	716
36	421	2.624			1.5		1.45	1.53	1.94	1.64	611	644	817	691
37	433	2.636			0.6	1.3	1.30	1.46	1.84	1.53	563	633	797	664
38	445	2.648		0.6	0.6		1.15	1.39	1.73	1.42	512	619	770	634
39	457	2.660		0.6	0.6	0.6	1.00	1.32	1.63	1.32	457	603	745	602
40	470	2.672	2.45	0.6		0.6	0.90	1.25	1.52	1.22	423	587	715	575
41	482	2.683		0.6	0.6		0.85	1.18	1.42	1.15	410	569	689	556
42	494	2.694		0.6	0.6		0.81	1.11	1.31	1.08	400	549	647	532
43	506	2.704		0.6			0.77	1.04	1.21	1.01	390	526	612	509
44	518	2.714			0.6	0.6	0.74	0.97	1.10	0.94	383	502	570	485
45	530	2.724	2.60		0.6		0.71	0.91	1.00	0.87	376	482	530	463
46	543	2.735		0.6	0.6		0.68	0.84	0.90	0.81	369	456	489	438
47	555	2.744		0.6			0.65	0.77	0.80	0.74	361	427	444	411
48	567	2.754					0.61	0.70	0.70	0.67	346	397	397	380
49	579	2.763		0.6	0.6	0.6	0.58	0.63	0.60	0.60	336	365	347	349
50	592	2.772	2.75				0.55	0.56		0.55	326	331		319
51	604	2.781			1.2		0.52	0.50		0.51	314	302		308
52	616	2.790		0.6			0.49			0.49	302			302
53	628	2.798					0.46			0.46	289			289
54	640	2.807					0.43			0.43	275			275
55	652	2.815	2.88	0.6			0.40			0.40	261			261
Sum				1000.2	998.9	999.6	999.9	999.6	1000.8	1001.67	63720	62252	66319	65050

On examining curve A, Fig. 9, it will be seen that this emulsion gives an extremely long range of sizes of grain so that with only about 1000 observations there are only a few observations for grains larger than about 1.75 in per diameter and the "contact" of the curve cannot be assigned very definitely. The curve is, therefore, very asymmetrical or "skew." The methods of sedimentation and centrifugal analysis, which are in progress of development will enable a larger amount of emulsion to be used in determining the grain size distribution curve, and it will then be possible to evaluate the statistical properties of the distribution—e. g., determine the mode and skewness—as far as possible.

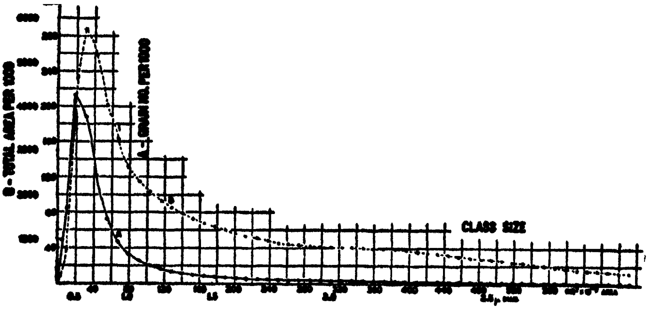

Fig. 9

TABLE X

Sample no.	Mean grain size mm² × 10⁻⁸		Mean equiv. diameter in μ		Standard deviation of area mm² × 10⁻⁸	
	a	*b*	*a*	*b*	*a*	*b*
1	53.7	63.7	.83	.90	174	361
2	52.2	62.2	.82	.89	174	332
3	54.9	66.3	.84	.92	174	317
Mean	53.6	64.1	.83	.90	174	337

In Table X the *mean* grain size, *mean* diameter and standard deviation from the mean size have been calculated for two cases,

a. a restricted range, to 30 classes, before gaps in the distribution appeared,

b. total range from the smoothed curves, hence including filled in values.

With respect to the terms used in Table X in summarizing the grain observations it may be noted that:

a. The range signifies the limits of grain size observed, extending in this case from $.2 \times 10^{-4}$ sq mm to 652×10^{-8} sq mm, i. e., a range of 1 to 3260 in areas or about 1 to 60 in equivalent diameters.

b. The *mean* grain size is the arithmetical mean of all the observed values; the equivalent mean diameter is calculated from this for a circle of equivalent area.

c. The *standard deviation* is the accepted measure for the dispersion or "spreading" of the observed values from the arithmetic mean and is calculated by the formula

$$\text{standard deviation } \sigma = \sqrt{\frac{\Sigma(\ x^2)}{n}}$$

where $\Sigma\ (X^2)$ is the sum of the squares of deviations of the grain sizes from the arithmetic mean, n, the number of grains measured. The more homogeneous or uniform the sizes of the grains are, the smaller the standard deviation will be, the less homogeneous they are in size, the greater it will be.

Summary

1. The methods of determining size-frequency distribution were classified and some of the methods previously used were described in detail.

2. A new comparatively quick but approximate method of determining size frequency of particles of silver halide in a photographic emulsion has been devised.

3. This method depends upon the sedimentation of the halide particles in equal portions of their suspension for increasing lengths of time, and after resuspending the sediments, counting in a haemacytometer the number of particles in each of them. At the same time, the weights of the various sediments are found by analysis of the supernatant liquids from each. By application of Stokes' law (Odén's method) or a modification of it, the size-frequency can then be determined.

4. A second more direct, but longer and more tedious method of determining size-frequency of the silver halide particles, was that of counting grains in random samples of emulsion which had been diluted and spread on a microscopic slide.

5. By means of a high-power microscope, and camera lucida the particles were drawn, and then were further magnified by projection, planimetered and classified.

6. A typical size-frequency curve obtained by the latter method was plotted for a high speed emulsion. A similar shaped curve was obtained by Mr. A. P. H. Trivelli. Also the curve plotted from Svedberg's work, had the same general shape.

In conclusion our thanks are expressed to Mr. Gordon Hoit for painstaking assistance in the experimental work.

Note: The following correction should be made to our previous paper in this Journal **25**, 191 and 194 (1920), Tables II and IV, 3rd, 5th, 7th, and 9th columns. The factor 10^5 should be substituted for 10^{-5}.

Rochester, N. Y.
May 12, 1921

NEW BOOKS

Applied Colloid Chemistry. General Theory. *By Wilder D. Bancroft. 20×14 cm; pp. viii + 345. New York: McGraw-Hill Book Company, Inc., 1921. Price : $3.00.*—In the far off days when the earth was comparatively young, the present reviewer remembers Professor Bancroft as a pioneer in the theory of heterogeneous equilibria and a virile revolter from the elegant triflings of the dilute solutionists. From those historical days up to the present time, there has always been a delightful quality of vigor and freshness about his work—something of the Norse Viking blowing in with the North wind on gentle shepherds in mellow valleys, or of Border Chieftains riding in the night with two-handed claymores. A quality, in short, of original strength, pleasantly spiced with humor and perhaps just a dash of original sin. Are not the pages of a certain well-known American scientific Journal strewn with the literary corpses of dull authors, and of the many who have erred in the fields of photochemistry, emulsions, adsorption, and colloids?

Professor Bancroft's many and excellent qualities are well exemplified in the present volume. There is something titanic about it. Read this from the Introduction:—"At first sight colloid chemistry may not seem to be an important branch of chemistry, either theoretically or technically; but this opinion changes when we consider that a knowledge of colloid chemistry is essential to anybody who really wishes to understand about: cement, bricks, pottery, porcelain, glass, enamels; oils, greases, soaps, candles; glue, starch, and adhesives; paints, varnishes, lacquers; rubber, celluloid, and other plastics; leather, paper, textiles; filaments, casts, pencils, and crayons; inks; roads, foundry cores, coke, asphalt; graphites, patines; zinc, phosphorus, sodium, and aluminum; contact sulphuric acid, hardened oils, etc.; beer, ale, and wine; cream, butter, cheese, and caseine products; cooking, washing, dyeing, printing; ore flotation, water purification, sewage disposal; smoke prevention; photography; wireless telegraphy; illuminants; comets; pharmacy; physiology. In other words colloid chemistry is the chemistry of every-day life." There you have the true Napoleonic glance. As Mallock said:

"Him not the splintered lightnings, nor the roll
Of thunders daunted, undismayed, his soul
Rose, and outsoared the thunder, plumbed the abyss,
And scanned the wheeling worlds from pole to pole."

That the present volume surveys the whole field in a characteristically original fashion will be evident from the titles of the chapters, which are as follows:—

I. Adsorption of Gas or Vapor by Solid.
II. Adsorption of Vapor by Liquid, and of Liquid and Solid by Solid and Liquid.
III. Adsorption from Solution.
IV. Surface Tension—Brownian Movements.
V. Coalescence.
VI. Preparation of Colloidal Solutions.
VII. Properties of Colloidal Solutions.

VIII. Jellies and Gelatinous Precipitates.
IX. Emulsions and Foams.
X. Non-aqueous Colloidal Solutions.
XI. Fog and Smoke.
XII. Gases and Solids in Solids.
XIII. Thickness of Surface Films.

In these chapters the author's liking for concrete facts and realities, and his very sparing use of mathematical formulae are in pleasant contrast with certain other works on the same subject. The book is packed with information and concisely written, so that it requires attentive and careful reading. The author makes no attempt to enter into any profound theorising or any great generality of theoretical treatment, but it may be fairly said that, if this constitutes any weakness, it is at the same time a source of strength. The title "Applied" would seem to indicate that the author has in view the "practical" man, who wants to know what colloid chemistry can do for him, and not what an author would like to do for—or with—colloid chemistry. If so, Professor Bancroft has succeeded admirably, and many men, both young and old, will thank him for it, and derive both pleasure and profit from the study of his book. The chapters on emulsions and foams, and on fog and smoke are valuable additions not hitherto dealt with in works on colloids, though their importance is very great.

All throughout the book the author's wide reading and knowledge of the subject are evident, though the condensed style of treatment—no doubt due to the great range of subject and the publisher's limit—is at times a little trying to the reader, who cannot always "wheel from pole to pole" with the celerity of the author. This remark does not mean that the treatment is anywhere inconsequent or illogical, but simply that the author's cornucopia of facts is great and generous.

The book forms an excellent complement to that other admirable one—Freundlich's "Kapillarchemie." One couldn't do better than read both books together. It would be like making friends with both the Norse Viking and the Gentle Shepherd.

F. G. Donnan

A Dictionary of Applied Chemistry. *By Edward Thorpe. Vol. I. Revised edition. 23 × 16 cm; pp. vi + 752. New York: Longmans, Green and Co., 1921. Price: $20.00.*—The preceding edition was got out with commendable promptness and apparently the same plan is to be followed with this one. The publishers, Messrs. Longmans, Green and Co., write that they expect to issue the second volume this summer and the subsequent ones at intervals spread over the next two years. That programme is all that anybody could ask.

The publishers also state that "the entire work has been carefully revised in the light of recent developments. Many new articles have been added and certain of the existing articles have been recast or wholly rewritten. Extensive additions have been made to subjects of technical importance, such as sulphuric acid, nitric acid, chlorine, alkali manufacture, synthetic production of nitrogen products, explosives, the synthetic coloring matters, the metallurgy of the commercially important metals, oils, fats, glycerine, etc. New articles appear on the natural organic coloring matters, and on the relation of color to chemical constitution. Fine chemicals have received special attention,

all the pharmacological articles have been revised, alkaloids and synthetic drugs have been treated at greater length and much new matter relating to them has been added."

Among the interesting topics in this volume are: acetic acid, acetone, acetylene, acidimetry, aconite, acridine dyes, actinium, adhesives, adrenaline, aerated waters, agate, alcohol, aldehyde, alizarine, aluminum, alums, amalgam, amber, amino-acids, ammonia, analysis, aniline, anthrocyanins, anthracene, antimony, argon, arsenic, asphalt, assaying, atmosphere, atomic weights, azines, azo dyes, bakelite, baking powders, balance, balata, balsam, benzene, bismuth, bleaching, blood, boiler incrustations, bone, boron, brandy, bread, brewing, bromine, butter, cadmium, caesium, caffeine, calcium.

Under acidimetry, p. 59, is given a table based on Thomson's work. It would have been better to have supplemented this with a table of pH values. The text of this article is unduly long because the remarks are kept vague. The article on adhesives, p. 76, is probably as good a one as could be written; but it brings out clearly our complete ignorance of the subject except on the empirical side. Under mineral waters, p. 83, the reviewer was interested to read that "the popular demand for a liquid which shall retain its frothy head for some time after it has left the bottle has led to the manufacturers frequently adding an extract of quillaia bark or other preparation of saponin, sold under the name of 'foam heading,' etc. Such an addition is more necessary in liquids containing saccharin than in all-sugar beverages, which froth more with the carbon dioxide."

Under balata is the statement, p. 529, that "in physical properties and chemical composition, balata resembles true guttapercha, for which it is the best natural substitute, and it is of interest in this connection that the trees yielding it belong to the same order as the trees which furnish guttapercha." Some of the rubber chemists say that the hydrocarbons of balata and guttapercha are identical and the reviewer would have welcomed a more definite stand on this point.

On pp. 11–16 there is a misprint in the headings: of acetanilide for acetic acid. Most of the articles are brief; but the editor has shown judgment in the matter. The longest article, as might have been expected, is the one on analysis, and the next longest is on the azo coloring matters. Others which run over four pages are: acetals, acetic acid, acetylene, acidimetry, aconitine, acridine, dyestuffs, aerated waters, alcohol, aldehyde, alizarine, aluminum, alums, ammonia, anthrocyanins, anthracene, antimony, assaying, atmosphere, azines, balance, barberry, barium, benzaldehyde, brewing, bismuth, bleaching, boiler incrustations, bone oil, brandy, Brazilwood, brewing, bromine, butter, butyl, calcium. Most of these are what one would expect; but the reviewer was surprised to find barberry in this list and he had not hitherto appreciated the importance of bone oil.

It is a great pleasure to find that a new edition of this important work is called for at the present time and that the need can be filled so promptly. Both of these things are very encouraging in the midst of the business depression.

Wilder D. Bancroft

Handbuch der anorganischen Chemie. *By R. Abegg and F. Auerbach. Vol. IV, Part 1, Second section. 25 × 17 cm; pp. xiii + 1072. Leipzig: S.*

Hirzel, 1921. Price: paper, 140 marks; bound, 170 marks.—From the preface it appears that work on this volume was begun again in 1918, which shows a promptness in getting back to work after the war that many of us may envy. The elements discussed in this volume are chromium, molybdenum, tungsten, and uranium. There are special chapters on the colloid chemistry of these metals and a very interesting one on what the authors call heteropoly acids, meaning phosphomolybdates, etc. The work done in getting out such a volume is enormous and the value to the chemist is correspondingly great. From a superficial reading the only thing that the reviewer missed was some statement about the ruby turning green when heated.

Each man will get different things from the volume according to his especial tastes. Among the things that interested the reviewer were: the effect of adsorption on the atomic weight of chromium, p. 6; the readiness with which chromic oxide changes to chromate when heated in presence of a trace of alkali, p. 8; the adamantine lustre of crocoite, p. 22; the hardness of chromium, pp. 30, 433; the reduction of hydroxylamine to ammonia by chromous salts, p. 51; the more recent data on the tin-chromium cell, p. 53; the pearly lustre of chromous fluoride, p. 56; the surface color of chromic bromide and oxide, pp. 102, 120; the electrolytic oxidation to chromate with lead peroxide anode, p 292; the effect of ultra-violet light on chromic acid solutions; p. 315, the equilibrium relations for chromium trioxide, p. 327; the color changes of lead chromate, p. 389; the problem of chromium dioxide, p. 398; the perchromates, p. 415; molybdenum blue, p. 626; Tammann's work on the physical properties of metals, p. 728; and tungsten blue, p. 821.

The question of the tungsten bronzes is an interesting one, pp. 834–837. One great trouble is the difficulty of analysis. It seems to the reviewer in his cheerful ignorance of the subject that most of this might be avoided by working synthetically. One could start with weighed amounts of WO_2, WO_3 and Na_2O; let them come to equilibrium; and examine for homogeneity. The weak point in this is, of course, that the mixtures might not reach equilibrium; but we do not yet know that and certainly this line of attack is more promising than the analytical one, which has broken down.

In the case of the phosphomolybdates, phosphotungstates, etc., it has been suggested that they are due in part to adsorption; but nobody seems to have tried the simple experiment of dialyzing some of these solutions.

Nobody has yet answered the question why the ruby is red. The most plausible explanation is that there are two forms of chromic oxide just as we know that there are two forms of chromic chloride; but the application of Werner's views to the ruby has not yet been made in any satisfactory way.

One might go on indefinitely, pointing out interesting things found in, or suggested by, this book; and others would make similar but entirely distinct lists. This would merely be giving additional proofs of what is already obvious, that the book is a monumental piece of work. *Wilder D. Bancroft*

Elementary Chemistry for Coal-Mining Students. *By L. T. O'Shea. 20 × 14 cm; pp. xi + 319. New York: Longmans, Green and Co., 1920. Price: $3.00*—In the preface the author says: "For many years I have delivered both popular and more or less systematic courses of lectures to deputies and other

workers in coal mines, students who have little or no knowledge of chemistry but are keenly desirous of learning something of the subject which may be useful to them in their daily occupation. The ordinary text-book of chemistry does not meet their requirements, for it contains much that it is unnecessary for them to study, and much that it is desirable for them to know is not to be found in it. The present work has been prepared with the object of meeting the wants of these as well as of other students of coal-mining. It is really a compilation of those parts of chemistry, pure and applied, that are cognate to the coal-mining industry, and does not pretend to be a textbook of chemistry."

The chapters of special interest to the coal-mining students are entitled: flame and the safety lamp; coal; by-products and their recovery; explosives; explosions in gases. The reviewer turned at once to the chapter on flames and was a bit disappointed to find on p. 130 that "to produce a flame it is necessary to have two gases in an active state of chemical interaction which will produce sufficient heat to raise the burning gas to a temperature at which it will give out light, or, in other words, becomes incandescent. Flame then is defined as a gas raised to incandescence by chemical interaction. All flames produced in air are caused by the chemical interaction of combustible gases with the oxygen of the air."

More successful are the paragraphs from the chapter on explosions in gases, p. 261. "In experiments made for the Prussian Fire-Damp Commission it was estimated that from 10 to 13 feet of flame are produced when a blown-out shot of half a pound of gunpowder is fired into gas-free air from a hot-hole stemmed with clay, and that the flame increases to 16 feet when the hole is stemmed with stone dust and coal dust, while if coal alone is used the flame increases to 31 to 52 feet. In experiments on flameless explosives made by the North of England Institute of Mining Engineers it was proved that considerably more flame was produced when shots were fired into dusty atmospheres than when fired into gaseous atmospheres without dust.

"When a gas explosion takes place it may be compared with a blownout shot, and if it occurs in a dust-free atmosphere the amount of flame produced is that due to the volume of gas that is burnt; but if the air be charged with coal dust the heat of the flame causes some of the dust to distill, with the production of gases which take fire and add to the volume of flame, while the atmosphere becomes charged with red-hot particles of coke dust.

"By far the most important effect is the manner in which coal dust will carry on a gas explosion beyond the limits of the gas-fouled areas. Many gas explosions have taken place which have traversed very considerable lengths of roadways, in some cases amounting to thousands of yards. The extent of the explosion in these cases is so great that it is difficult to account for it by the explanation that the atmosphere throughout the course of the explosion was fouled with gas in sufficient quantity to form an explosive mixture. If this were so, there would be evidence of alarm all along the course, but in most cases this is wanting. It is also improbable from the fact that generally the roadways are main intake air-ways, which could only be fouled by gas coming from some sudden outburst.

"These main intakes are generally dry and dusty with coal dust which forms tolerably thick layers on the roadways, timbers, and walls, and in its

finest form floats in the air itself. The dust in such an atmosphere produces just the conditions necessary to continue an explosion of gas when started, for, when the explosion takes place, the flames not only shoot forward into the dusty atmosphere and ignite the dust in suspension, but the vibrating masses of burning gas blow up clouds of dust in front of them which become ignited, and they in turn blow up and ignite further clouds and the explosion is continued along the dusty roads as long as there is coal dust in sufficient quantity capable of being blown up into the air by the force of the exploding mass.

"In these explosions it is a well-known fact that their course is stopped by roadways that are wet, from which the dust cannot be blown up in clouds, or roadways dusty with a non-inflammable stone dust, or coal dust largely mixed with stone dust, which proves that coal dust and not gas causes the propagation of the explosion. If the explosion were continued in an atmosphere fouled with gas along its whole course the wetness of the coal dust or the presence of stone dust would make no difference to the explosion, which would continue so long as there was gaseous fuel, and only the absence of gaseous fuel would stop it, whereas in an explosion propagated by coal dust it is the absence of inflammable dust that stops the explosion." *Wilder D. Bancroft*

Applied Electrochemistry and Metallurgy. *By Charles F. Burgess, H. B. Pulsifer and Benjamin B. Freud. 21 × 14 cm; pp. 198. Chicago: American Technical Society, 1920. Price: $2 50.*—Professor Burgess has written the section on applied electrochemistry and Messrs. Pulsifer and Freud the section on metallurgy. The scope of the book is given in the introduction.

"The principles of Electrochemistry are almost as old as the science of electricity itself. The phenomenon of electrolysis was discovered in 1800, and its laws were experimentally determined by Faraday in 1833; again the electrolytic cell, with its simple electrodes and conducting liquid, was very early used to accomplish the dissociation of chemical compounds in the same manner as it is now used in chemical industries; the electric furnace was really discovered almost simultaneously with the arc lamp and in its essentials is identical with it.

"The cheapening of electrical power and the increased use of the products involved have been largely responsible for the progress along these lines, and today, the preparation of electrolytic copper is a great industry; hydrogen and oxygen gases are now obtained by the electrolytic decomposition of water; and the method of electrolyzing fused aluminum oxide has brought the price of aluminum to a practical basis. Again, by means of the electric furnace, several highly resisting chemical reductions have been accomplished and methods have been perfected for the manufacture of calcium carbide, silicon products, carborundum, graphite, and steel.

"The same years that have seen such remarkable progress in Electrochemistry, have also witnessed uncommon development in that closely related art—Applied Metallurgy. The great steel works of the country, the coal and iron-mining industries, ship-building, ordnance manufacture, sky-scraper erections and hundreds of other fields, are hugely interested in what the skilled metallurgist discovers. Metallurgy and Electrochemistry alike attract students—following through processes in these arts at times attains the interest of a novel.

"Finally, when by the aid of intense electrical discharges in air, even the nitrogen of the atmosphere is made available for our use, the results seem to approach the miraculous. To think of the world's supply of nitrates being augmented from the very atmosphere itself seems more like a dream of a Jules Verne or a Wells, than an actual twentieth century accomplishment.

"All of these scientific marvels are intensely interesting and the treatment has been made exceedingly practical by the authors. The material is written in a clear readable style and is designed to appeal to both the trained engineer and the layman. It is the hope of the publishers that a study of this volume may widen the acquaintance of many readers with this branch of industrial electricity and stimulate their interest in the general scientific development of the world."

It is intended to be a popular book and it gives a sketchy but fairly satisfactory presentation of the subject. The reviewer had supposed that in the Birkeland-Eyde process the air travelled through the disc of flame and not parallel with it, p. 81. *Wilder D. Bancroft*

Die Schwimmaufbereitung der Erze. *By Paul Vageler. 23 × 16 cm; pp. v + 98. Dresden and Leipzig: Theodor Steinkopff, 1921 Price: 4 shillings, 4 pence.*—The subject is treated under the general headings: historical sketch of the theories; the effective forces in ore flotation; the mechanism of the processes taking place in the ore-pulp; practical points of view for carrying out flotation rationally; account of the more important methods for examining ores and reagents; account of the more important methods in technical use. Nothing could be better than this programme and our interest is excited by the author's statement that the German method of scientific study clears up matters in a way that is impossible by the Anglo-Saxon method of cut-and-try.

Unfortunately the promise of the table of contents is not fulfilled in the text. The author is quite clear that the contact angle is a less important factor in ore flotation than adsorption; but we did not need a German to tell us that. There is a good deal about Werner's co-ordination theory in the book but very little that is helpful in regard to ore flotation. There is no adequate discussion of the conditions under which froth is formed or is stable; there is no comparison of the Callow process with the orthodox 'bubbles' process; the question of soluble and insoluble frothing agents is not taken up seriously; there is no explanation why saponin kills flotation under ordinary conditions or why adding copper sulphate to the Tennessee zinc ore was beneficial.

The author is very vague in his statements and about all that the reviewer has got out of the book is that ore to be treated by flotation should all pass a 60-mesh sieve and 75 percent of it should pass a 200 mesh sieve. The reviewer is inclined to believe that even that was found by a cut-and-try method and is not a triumph of German sagacity. The author believes that ore flotation may perhaps be superseded some day by differential sedimentation; but he does not go into details. *Wilder D. Bancroft*

Physical Chemistry for Colleges. *By E. B. Millard. 21 × 15cm; pp. vii + 411. New York: McGraw-Hill Book Co., Inc., 1921. Price: $3.50.*—In the preface the author says: "This book has been prepared to bring before college

students certain of the more important aspects of physical chemistry, together with accurate modern data which illustrate the applicability of its laws to the phenomena observed in the laboratory. It has been assumed that the student is familiar with inorganic and analytical chemistry, that he has had an adequate course in college physics, and that the simple processes of calculus are familiar to him.

"No attempt has been made to cover the whole of physical chemistry in a single volume; its most important topics have been treated at such lengths as the size of the volume allows, and numerous references to recent periodical literature are included for those who would pursue any given topic further.

"The limitations of the orthodox laws of physical chemistry have been emphasized more than is commonly done in beginning courses of physical chemistry. To this end the illustrative data have been carefully chosen from modern experimental work, in order to minimize the "experimental errors" which are so often used to conceal real deviations of a law from the facts it is intended to express. A trusting belief in inadequate physical laws will only retard the scientific progress of a student, and weaken his faith in adequate laws; whereas a wholesome appreciation that physical chemistry is an unfinished and growing science may stimulate thoughtfulness and research. The proper time to encourage a research attitude is in the very beginning of a student's chemical career."

The chapters are entitled: introduction and determination of atomic weights; laws of gases; liquid substances; solids; solutions—ideal solutions; ionized solutes and electrical conductivity; thermochemistry; homogeneous chemical equilibrium; heterogeneous chemical equilibrium; velocity of chemical reactions; physical properties and chemical structure; the periodic law; radiochemistry and radioactivity; surface chemistry—colloids; electrochemistry—electromotive force.

There are a number of good things in the book: the diagram for gases, p. 25; the comparative table for internal pressures, p. 67; the diagram for the change of atomic heat capacity with the temperature, p. 97; the half-tone for the X-ray patterns of sodium fluoride and sodium hydrogen fluoride, p. 104; the table for the hydration of ions, p. 182, though some reference to Bousfield should have been made; the comparison of activity coefficients and conductance ratios, p. 183; the phase diagram for urethane, p. 274.

On p. 89 the author discusses Langmuir's views on the spreading of oil on water and on p. 107 Langmuir's ideas on adsorption. He might well have pointed out that Langmuir has deduced an equation for the adsorption isotherm on the explicit assumption that the adsorption layer is several molecules thick. On p. 118 the author fails to bring out that an aqueous solution saturated with sodium chloride will not be in equilibrium with a saturated solution of sodium chloride in alcohol. The relation is also not true if we substitute ether for alcohol though the error is much less. On p. 156, under chemical reactions at the electrodes, the author italicizes the statement that "the reaction requiring the lowest potential always takes place first." This is true provided one knows how to interpret it; but there is no reference anywhere to overvoltage and it will be difficult for the student to see why cadmium should precipitate on platinum from an acidified cadmium sulphate solution. The reviewer was interested in a statement on p. 123. "The large errors in the pressure of carbon disulphide calculated

by means of Raoult's law when it is present in small proportion illustrate an important fact. Raoult's law is a law for the vapor pressure of a solvent, and carbon disulphide is scarcely the solvent when its mol. fraction is only $1 - 0.885 = 0.115$." The reviewer is quite willing to accept this; but the definitions of solvent and solute should be adjusted to suit. The reviewer would also have liked to have seen a few remarks about volume concentration versus mass concentration and about heats of dilution.

The author is quite explicit, page 175, as to the difficulty in regard to the change of the transference number with the concentration. "The transference number of an ion is the fraction of the total electricity carried by it through a solution. A table of such transference numbers for the positive ions in solution is shown in Table 71. It should be noted that these transference numbers change but little with the temperature, in spite of the large increase in equivalent conductivity at higher temperatures mentioned on page 178. This means that all ions increase their velocities at about the same fractional rate as the temperature is raised, but there is a slight change in ionic velocity ratio with concentration, which lacks an explanation as yet. If the ions moved through solutions at the same rate as through pure water there should be no such change; it is commonly ignored in calculations, but is still one of the unsolved problems of physical chemistry. A possible cause of the change is that one ion combines with more water than the other, thus increasing its size and decreasing its velocity. There is definite proof that the ions are combined with considerable water and it is reasonable to suppose that the extent of this solvation changes with the proportion of water available, and with the temperature."

On p. 369, under colloids, the author says that "viscous emulsions and gels have the same structure; a stiff jelly is often convertible into an emulsion by heating, and it returns again to the state of jelly after cooling. In each case microscopic droplets of one liquid phase are completely surrounded by a continuous film of the other liquid phase. It is not necessary that the continuous phase be present in greater quantity than the dispersed phase; a cross-section of an emulsion in which the disperse phase is present in excess might look something like a section through a cake of honey, with thin films of continuous phase (represented by the wax cell walls) surrounding droplets of dispersed phase." The reviewer would be quite satisfied if he could prove which jellies had a honeycomb structure.

Wilder D. Bancroft

A Dictionary of Chemical Solubilities. Inorganic. *By A. M. Comey and Dorothy A. Hahn. Second edition. 22 × 15 cm; pp. xviii + 1141. New York: The Macmillan Company, 1921. Price: $14.00.*—When the first edition appeared the reviewer criticized it (**1**, 53) as typical of everything that was bad. It is a pleasure to note that the second edition is a distinct improvement in many respects. Limits of solubility are now given in many cases and attention is paid very often to the nature of the phase which crystallizes. There has not been any complete revision in regard to these points. On p. 144, for instance, we read that anhydrous calcium chloride is soluble in 1.58 parts of water at 10.2°. Everybody knows that this is not so and everybody knows that what Kremers found was that the solution saturated with respect to $CaCl_2.6H_2O$ contains one part of anhydrous calcium chloride to 1.58 parts of water. The editors have not

distinguished between the perfectly proper method of stating the analytical data and the absolutely improper method of stating the solubility. In this particular case there is no harm done because everybody recognizes the error; but it rather leaves one up in the air as regards less familiar substances. While on this point the reviewer protests against the statement that anhydrous calcium chloride is very soluble in water with evolution of heat. The formation of hydrated calcium chloride is accompanied by an evolution of heat but both anhydrous and hydrated calcium chloride are more soluble with rising temperature and therefore dissolve with absorption of heat.

Because people speak of iron dissolving in sulphuric acid, statements of this sort are included even in the second edition, though of course no solubility can be given. The weird alphabetical arrangement is continued. The reviewer thinks that there are probably data on hydrobromic acid somewhere in the book; but he could not find them.

The book is valuable on account of the immense amount of data in it; but the size has doubled and the cost has nearly trebled. Under the circumstances it would have been better if the editors had cut out a great deal of the dead wood and had presented the data in the best possible way. It is hard to believe that it would have taken more work to have revised the book well than to have revised it badly. The publishers should have insisted on the work being done properly. While the volume will be a necessity in every library, the wildest flight of imagination cannot make it a credit to American chemistry. *Wilder D. Bancroft*

Handbuch der Mineralchemie. *By C. Doelter. Vol. 3, Part 6. 26 × 19 cm; pp. 164. Dresden: Theodor Steinkopff, 1918. Price 78 cts.*—This number contains native bismuth and the oxides of bismuth, vanadium, the uranium-vanadium and the vanadium-silica minerals, and water. The reviewer was interested in the statement, p. 816, that the crystallized oxide of bismuth has a pearly to adamantine lustre. Some sort of real classification of lustres should be made and if neither the physicist nor the mineralogist will do it, it is apparently a problem for the physical chemist and the psychologist. The fact that carnotite occurs in this number will make it of interest to many people.

Sixty pages are given up to a discussion of water, which at first sight seems out of place. No special justification is offered for including it, except that water occurs commonly on the earth. If one waives the question of appropriateness, it is certainly a good thing to have accessible the compilation of data which Kremann has presented. He gives the data for: the equilibrium constant; the electrolysis; the electrolytic dissociation; water as solvent; hydroylsis; hydrogen peroxide; catalytic action; phase diagram; vapor pressure curve; boiling-point; rate of vaporization; heat of vaporization; heat of fusion; melting point curve for ice; varieties of ice; volume relations; specific heat; viscosity; index of refraction; electrical double refraction; surface tension; molecular constitution; and water of crystallization. The remaining twenty-five pages are given up to a discussion of natural waters. *Wilder D. Bancroft*

THE NATURE OF SECONDARY VALENCE

BY HOMER W. SMITH

PART III—PARTITION COEFFICIENTS IN THE SYSTEM WATER: ETHER

§ 1. Introduction

In the preceding paper a method of correction was given which was designed to eliminate the disturbing influences of dissociation, association, etc., from partition coefficients. This method of correction consisted in plotting the ratio C_2/C_1 against C_2 (where C_2 and C_1 are the concentrations of the solute in the organic solvent and the water layers, respectively), and interpolating the value of C_2/C_1 when C_2 has a given unitary value, such as 1 millimol per litre. The value of the ratio C_2/C_1 so obtained was called the partition coefficient, $\mathfrak{P}$. The partition coefficients of a large number of organic acids and bases were determined for the systems water: xylene and water: chloroform.

It was shown that if the logarithms of the partition coefficients, $\mathfrak{P}$, for various molecular species were plotted against their respective volumes, the observed points fell into several straight and parallel lines, these lines being separated from each other along the ordinates by arithmetically equal values of $\mathfrak{P}$. The compounds which fell upon a given line were arbitrarily called a "series."

Ether was chosen for further work in partition coefficients largely because of its solubility in water. At 25°, water dissolves about 6 percent by weight of ether, and ether dissolves about one percent of water. This is nearly ten times the mutual solubility of water and chloroform. Thus the use of ether makes it possible to observe the extent to which the mutual solubility of the solvents affects the comparative results. Furthermore, ether is a good extractive of the organic acids and it is possible to study many compounds hav-

ing very low partition coefficients which could not be studied in the systems previously used.

The ether was carefully repurified by distilling over calcium chloride and calcium oxide. Equal volumes of ether and of the aqueous solutions of known titer were measured into graduated flasks, and then mixed and shaken in separatory funnels after having been brought to the correct temperature. Samples of the water phase were than withdrawn and titrated, and the concentration in the ether was determined by difference. The solutes were taken from the samples used in the previous systems without further attempts at purification.

2. General Considerations

The relations disclosed by the partition coefficients in the system water: ether are essentially like those previously discussed for the systems water: xylene and water: chloroform:

1. The observed points fall into several straight and parallel lines.
2. These lines (or series) are separated from each other by distances along the ordinates which are arithmetically equal (equal intervals of $\mathfrak{P}$), except that—
3. Since $\mathfrak{P}$ is a logarithmic function of molecular volume, the value of the interval separating any two corresponding series increases ten times with each increase in the absolute value of $\mathfrak{P}$.
4. The equation covering these straight line relationships has been previously given:

$$\text{Log}\,100\,\mathfrak{P} = \frac{V_m}{60.00} \pm a$$

(V_m is the molecular volume and *a* has been arbitrarily called the "series constant.")

The data for the partition coefficients in the system water: ether have been given in the following tables. They are

arranged by series (*i. e.*, those compounds falling in the same line) beginning with the highest observed series and passing regularly to the lowest. The logarithmic nature of this series progression results in the separation of the series by actual (or graphical) intervals which gradually diminish in a repetitive fashion, each group of eight series comprising an increase of ten times in the value of p at a given volume. Consequently each series within one of these groups of eight[1] may be said to occupy a characteristic position, denoted by the "series number." This series number is derived directly from the series constant. As an illustration consider the first ten series given in Table II.

Series constant a	Antilog. of a	Series number
+1.41160	25.80	4.0 x 6.45
+1.28666	19.35	3.0 x 6.45
+1.11057	12.90	2.0 x 6.45
+0.80954	6.45	1.0 x 6.45
+0.71263	5.16	.8 x 6.45
+0.65464	4.515	.7 x 6.45
+0.58769	3.87	.6 x 6.45
+0.50851	3.225	.5 x 6.45
+0.41160	2.58	.4 x 6.45

The figures in the second column are related to each other as integral multiples of 6.45: hence the respective series may be most simply indicated by this multiple, or "series number," as given in column 3. These series numbers have been given a decimated form in order that their relative position may be identified more readily. That is, the series above the first series 1 have been numbered with integrals, the next group with tenths, the next with hundredths, and so on. This arrangement will be made clearer by reference to Figure 1.

[1] The term "octave" was previously applied to each group of eight intervals, but it was based upon the erroneous idea that there were only eight possible series; this point is refuted in this paper and hence the term has been abandoned.

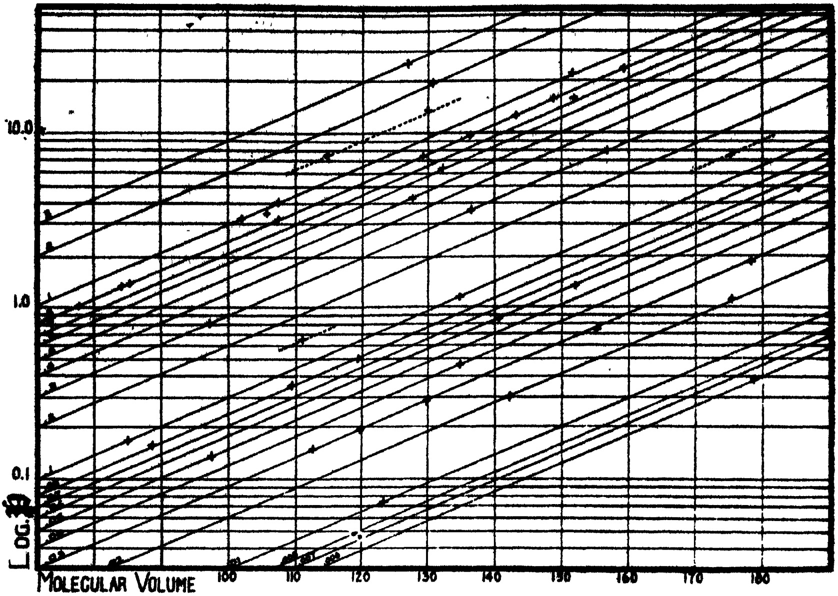

Fig. 1.—The Partition Coefficients ($C_2 = 1$ m/L) in the System Water: Ether

TABLE I

Partition Coefficients of the Amines

Water: Ether

Series no.	a	V_m	C_2	𝔓 obs.	𝔓 calc.
1.	+0.39794				
	Methyl amine	43.0	1	0.113?	0.132
	Trimethyl amine	88.0	1	0.660?	0.732
.8	+0.30103				
.7	+0.24310				
	Dimethyl amine	66.3	1	0.231	0.224
.6	+0.17609				
	Ethyl amine	64.6	1	0.172	0.179
	n-Butyl amine	106.8	1	0.905	0.905
	iso-Amyl amine	127.0	1	2.02	1.96
	Benzyl amine	127.4	1	2.00	1.99
	Benzyl methyl amine	151.0	1	5.00	4.93
	n-Heptyl amine	169.5	1	10.3	10.03
	Benzyl ethyl amine	173.0	1	11.6	11.46
.5	+0.09691				
	Dipropyl amine	151.5	1	3.86	4.18
.4	±0.00000				
	Piperidine	108.8	1	0.655	0.651
	Diethyl amine	109.3	1	0.652	0.663
	n-Methylpiperidine	133.8	1	1.68	1.70

TABLE II
Partition Coefficients of the Acids
Water: Ether

Series no.	a	V_m	C_2	$\mathfrak{P}$ obs.	$\mathfrak{P}$ calc.
4.	+1.41160				
	Benzoic acid	126.9	10	33.0	33.6
3.	+1.28666				
	Benzoic acid		1	25.0	25.2
2.	+1.11057				
	Chloroacetic acid	75.0	100	2.5	2.58
	α-Bromopropionic acid	105.8	10	7.4	7.48
	β-Iodopropionic acid	115.0	10	10.0	10.65
	Salicylic acid	130.6	1	19.0	19.37
	Resorcinilic acid	136.3	10	23.0	24.11
1.	+0.80954				
	Formic acid	41.5	1	0.320	0.317
	α-Crotonic acid	102.1	1	3.20	3.24
	α-Bromopropionic acid	105.8	1	3.48	3.74
	n-Butyric acid	107.8	1	4.05	4.04
	p-Oxybenzoic acid	132.3	10	10.2	10.34
	o-Nitrobenzoic acid	150.8	1	2.17	2.103
.8	+0.71263				
	Thiacetic acid	73.6	1	0.84	0.869
	Chloroacetic acid	78.0	1	1.02	1.03
	Bromoacetic acid	84.5	1	1.32	1.37
	Propionic acid	85.3	1	1.32	1.36
	sec-Butyric acid	107.3	1	3.22	3.17
	iso-Valeric acid	129.5	1	7.40	7.43
	Resorcinilic acid	136.3	1	9.40	9.64
	Gentisinic acid	136.5	10	10.3	9.72
	o-Chlorobenzoic acid	143.3	1	12.5	12.60
	Phenylacetic acid	148.9	1	15.2	15.60
	o-Iodobenzoic acid	159.4	1	23.0	23.40
.7	+0.65464				
	Acetic acid	64.0	1000	0.535	0.526
	Dichloroacetic acid	97.2	10	1.9	1.882
	m-Nitrobenzoic acid	151.9	1	15.5	15.4
.6	+0.58769				
	Acetic acid	64.0	1	0.450	0.451
	p-Oxybenzoic acid	132.3	1	6.2	6.20
.5	+0.50851				
	α-β-Dibromopropionic acid	127.8	1	4.20	4.35

TABLE II (*Continued*)

Series no.	a	V_m	C_2	φ obs.	φ calc.
.4	+0.41160				
	3.5-Dinitrobenzoic acid	175.8	10	21.0	21.96
.3	+0.28666				
	Dichloroacetic acid	97.2	1	0.805	0.8066
	Gentisinic acid	136.5	1	3.6	3.64
.2	+0.11057				
.1	—0.19046				
	Pyruvic acid	85.3	1	0.162	0.170
	Anthranilic acid	135.0	1	1.11	1.147
	Oxalic acid	75.6	10	0.116	0.119
	Lactic acid	88.7	10	0.191	0.194
	Bromosuccinic acid	140.5	10	1.38	1.417
.08	—0.28737				
	Oxalic acid	75.6	1	0.092	0.094
	Lactic acid	88.7	1	0.155	0.155
	β-Oxybutyric acid	109.7	1	0.353	0.348
	Trichloroacetic acid	119.5	1	0.495	0.506
	Mandelic acid	152.2	10	1.66	1.775
	Acetylsalicylic acid	185.6	10	6.7	6.397
.07	—0.34536				
	2.4-Dinitrobenzoic acid	175.3	10	3.6	3.77
.06	—0.41231				
	Bromosuccinic acid	140.5	1	0.84	0.85
	Mandelic acid	152.2	1	1.30	1.33
	Acetylsalicylic acid	185.6	1	4.75	4.80
.05	—0.49149				
	Malonic acid	97.8	1	0.134	0.1376
	Benzilic acid	238.3	10	31.8	30.21
.04	—0.58840				
	Gallic acid	135.0	1	0.451	0.4588
.03	o-Phthalic acid	155.6	10	1.04	1.072
	—0.71334				
	Maleic acid	112.6	1	0.150	0.1457
	Succinic acid	120.0	1	0.192	0.193
	Laevulinic acid	130.0	1	0.280	0.284
	o-Phthalic acid	155.6	1	0.740	0.758
.02	Benzilic acid	238.3	1	18.0	18.1
	—0.88943				
	Glutaric acid	142.2	1	0.296	0.302
.01	2.4-Dinitrobenzoic acid	175.3	1	1.10	1.08
	—1.19046				
.008	Tartaric acid	123.6	1	0.072	0.0740
.007	—1.28737				
	—1.34536				
.006	2.4.6-Trinitrobenzoic acid	197.0	10	0.88	0.867
	—1.41231				
.003	Hippuric acid	178.7	1	0.379	0.368
	—1.71334				
	2.4.6-Trinitrobenzoic acid	197.0	1	0.36	0.371

TABLE III

The Evaluation of Series Which Are Not Integrally Related

	V_m	C_2	p obs.	*a* calc.	Series no. corre-sponding to *a*
Ether					
Formic acid	41.5	10	0.430	+0.94181	
Bromoacetic acid	84.5	10	2.27	+0.94770	
n-Butyric acid	107.8	10	5.20	?(+0.91767)	
β-Iodopropionic acid	115.0	1	7.3	+0.94666	
n-Valeric acid	130.0	1	13.54	+0.96464	
m-Nitrobenzoic acid	151.9	10	31.00	+0.95970	
			Mean	+0.95210	1.388
α-Oxybutyric acid	111.2	1	0.633	—0.05193	
3.5-Dinitrobenzoic acid	175.8	1	7.7	—0.04351	
			Mean	—0.04772	.1389
Chloroform					
β-Oxybutyric acid	109.7	1	0.196	—0.53607	.1353
Xylene					
n-Caproic acid	152.5	1	2.37	—0.16691	1.588
			Mean for Series no.		1.406
Ether					
Chloroacetic acid	78.0	10	1.58	+0.89866	1.227
Fumaric acid	112.6	1	0.58	—0.07556	.1190
Xylene					
iso-Caproic acid	152.0	1	1.75	—0.29029	1.192
			Mean for Series no.		1.203
Ether					
Trichloroacetic acid	119.5	10	1.50	+0.18443	.237

There are ten instances which clearly indicate the existence of a series midway between Series 1 and 2. The exact value of this series has arbitrarily been placed at 1.414, or the square root of two (obs. 1.406). There are three instances indicating the existence of another series between this and Series 1, which have the average value 1.203. The remaining compound, trichloroacetic acid, falls between Series .2 and .3 (obs. .237). The last two cases will be disregarded for the

time being, but the evidence is sufficient to establish the existence of a series between Series 1 and 2, and in subsequent discussions this will be recognized as Series 1.414.

3. The Interpolation Value of C_2

In the previous communication only those partition coefficients were considered which were derived by interpolating to one millimol per litre in the organic solvent. Though a detailed discussion of the method of correction cannot be attempted at this time, it may be pointed out that this method is of such a nature that the general interpretation should be no different were it based upon results obtained from interpolations to any other series of geometrically related values, such as 10, 100 or 1000 millimols per litre. (For that matter, one might choose any geometrically related series of numbers such as 2, 20, 200, etc., 3, 30, etc., for the interpolation concentrations.) Practical difficulties prevent the determination of distribution ratios for many substances at such concentrations that we may interpolate to 1000 or even 100 m/L, but in the majority of instances it is possible to make this interpolation to 10 m/L. At the time this experimental work was done it was not intended to make such an interpolation, and consequently it is possible to do so on only a part of the available data. These values, derived from 10 m/L, are included in the preceding tables. The figures in the third column give the value of C_2 to which interpolation has been made.

4. The Inter-relations of Series

On the basis of the results obtained in the systems water: xylene and water: chloroform it was stated that the observed values of $\mathfrak{P}$, when plotted against molecular volume, fell into parallel lines or series which are separated from each other by distances (in terms of $\mathfrak{P}$) which *are related as the integrals from one to 10*. (Series 9 apparently is missing.) This statement, though well supported by the evidence under consideration, must be modified in view of the evidence furnished by the system water: ether. This latter evidence shows that

there are series which are not taken into account by this simple integral relationship. The data bearing upon these additional series are given in the following table.

The series constants *a* which are given in the fourth column have been calculated from the observed partition coefficients. The series number is obtained from these series constants by subtracting the value of *a* for Series 1, and converting the difference to the antilog. Some additional data have been included from the systems water:xylene and water: chloroform.

5. The Blank Series

In ether, as in xylene and chloroform, some series appear to be more favored than others, so far as the number of observed cases occurring in them is concerned. Thus the number of compounds occurring in the various series is as follows:

Series numbers				Acids $C_2 = 1$ m/L	$C_2 = 10$ m/L	Amines $C_2 = 1$ m/L
1	.1	.01		8	4	2
2	.2	.02		2	4	0
3	.3	.03		9	4	0
	.4	.04		1	3	3
	.5	.05		2	1	1
	.6	.06	.006	6	0	7
	.7	.07		1	4	1
	.8	.08		14	3	0

Considerable emphasis was previously laid on the fact that some of these series, though theoretically called into existence by their simple inter-relationships, were apparently blank, in the sense that no compounds were observed in them. The existence of these so-called "blank series" is not borne out by this study. Thus among the acids at $C_2 = 1$ m/L, Series 2, 4, 5 and 7 contain the smallest number of compounds, whereas among the amines, the minima are Series 2, 3, 5, 7 and 8. In xylene and chloroform, Series 5, 7 and 8 were blank with both the amines and the acids. Thus there is a tendency for the amines to congregate in the same series in xylene, chloroform and ether; but with the acids, if any

series at all may be considered as favored in ether, they are certainly not the same as those favored in xylene and chloroform. It is evident that we cannot describe any series as being definitely blank, but that the appearance and identity of such series depends upon the particular solvents under consideration. However, the point that some series may be differentiated from other series under particular conditions, cannot be held to be without significance in view of the relations previously discussed in this connection[1] though the reason for this differentiation is not evident at the present time.

6. The Absolute Values of the Series Constants

The series constants in the system water:ether (a_e) are related to the series constants in the system water:xylene (a_x) by a constant difference:

$$\text{(Acids) } a_e = a_x + \log 15.0$$
$$\text{(Amines) } a_e = a_x + \log 1\ 50$$

Thus each series in the system water:ether has a value in terms of [illegible], at a given molecular volume, just 15.0 or 1.5 times its value at that same volume in the system water:xylene.[2]

The exact value of any series constant in this, as in other cases, is theoretically determined by extrapolating from the observed points to $V_m = 0$ according to Equation I. But it could not be expected that such a method would yield outright a pure integral relationship such as 15.00; it must be admitted that this evaluation is based upon the assumption that the series constants for various solvents are also integrally related. It may be reiterated here that a similar integral relation existed between the systems water:xylene and water: chloroform;

$$\text{(Acids) } a_c = a_x + \log 5\ 00$$
$$\text{(Amines) } a_c = a_x + \log 5.00$$

Other systems containing water will be considered later, when it will be seen that this integral relationship is just as true for various solvents as for the solutes.

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[1] Jour. Phys. Chem., 25, 160, 204 (1921).

[2] The system water: ether is the only one in which the acids and amines behave differently in this respect. It is noteworthy that here the difference is exactly 10 to 1.

Summary

The partition coefficients of 49 organic acids and 15 organic bases have been determined in the system water:ether at 25°. The results obtained from a comparative treatment of these partition coefficients in terms of molecular volume are in good agreement with the results obtained in the systems water:xylene and water:chloroform. For a detailed discussion on these results, the reader is referred to the previous communication.[1]

It is realized from the consideration of further evidence that the interpretation of these results may have to be modified in some respects, but no attempt will be made in this direction until all the experimental evidence has been presented.

[1] Jour. Phys. Chem., **25**, 160, 204 (1921).

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THE NATURE OF SECONDARY VALENCE

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Supplementary Note on the Method of Correction

The recognition of series other than the eight which have been hitherto considered raises a question as to the fundamental nature of this rhythmic behavior and the validity of the interpretation based upon it. No entirely satisfactory answer can be made at the present time, but a careful consideration of the evidence discloses something of the nature of the phenomena with which we are dealing.

In the first place it can be seen from the data which have been given that in passing from concentrated to dilute solutions, the partition coefficient moves progressively through one or more series. A few examples are given below.

	C_2	Series number	$\mathfrak{P}$ obs.	$\mathfrak{P}$ calc.
ETHER				
Dichloroacetic acid	10	.7	1.9	1.88
	1	.3	0.805	0.806
Oxalic acid	10	.1	0.116	0.119
	1	.08	0.092	0.094
Chloroacetic acid	1000	2.	2.5	2.58
	1	.8	1.02	1.03
CHLOROFORM				
Acetic acid	1000	1.0	0.25	0.25
	100	.4	0.10	0.1002
	10	.1732 (1)	0.438	0.4322
	1	.1	0.025	0.025
Chloroacetic acid	1000	.3	0.125	0.1287
	100	.1414 (2)	0.062	0.0620
	10	.08	0.0342	0.0343
	1	.04	0.0168	0.01716

(1) $0.1732 = \sqrt{\bar{3}}$
(2) $0.1414 = \sqrt{\bar{2}}$

In the second place, the distribution ratios for many substances are essentially constant during dilution. (Cf. acetic, anthranilic, sec-butyric acids, etc., in the following experimental section.) In the third place, there are instances in xylene and chloroform where the distribution ratio increases with dilution. (Cf. *iso*-amylacetic acid, ethylamine and methylamine, etc.)

Nevertheless, by interpolating at geometrically related points in these processes, we obtain values which are consistently related in a regular manner. In these processes, we are dealing with a stoichiometric complex (association, dissociation, hydration, etc.), which "decomposes" at a given rate as we pass from concentrated to dilute solutions. If we look upon this decomposition, expressed in the ratio C_2/C_1, as exponential in character, then by means of the geometrically related interpolations which we are making we are cross-sectioning the "behavior," so to speak, of various molecular species under comparable conditions. The fact that the relation C_2/C_1 is never of a type which can be covered throughout all dilutions by a single exponential equation has been repeatedly demonstrated. Where one exponent covers it through a given range, another exponent must be used to cover it through an adjacent range. In order to cover the entire range from very concentrated to very dilute solutions, it would be necessary to assume transitions from one exponent to another;

$$C_2/C_{x_1} = a; \quad C_2/C_{y_1} = b; \quad C_2/C_{z_1} = c; \text{ etc.}$$

The fact that this interpolation treatment reveals such simple arithmetic relations in relative solubility and stoichiometric behavior would indicate that similar arithmetical relations exist in those forces which give rise to the stoichiometric complex. (In view of the existence of non-integral series such as 1.414, etc., it is perhaps unwise to use the term *integral* in this connection; but the same idea is conveyed and the facts more accurately described, by the term *simple, arithmetical* relations.)

As a matter of fact, the interpolation treatment *could not* yield intelligible results were the initial forces in the stoichiometric complex continuous, instead of discontinuous, variables; nor, if these forces were continuous variables, could it be directly demonstrated that molecular volume played any rôle in intermolecular relations, for if there is to be *more than one series*, the various series must be separated by at least *definite*, if not *related*, amounts.

And in view of our present notions of the structure of matter, it is not difficult to believe that the various degrees in discontinuity in the fundamental forces are related in some simple manner.

SECTION III

Experimental[1]

Note of Correction.—The data for the partition of acetic and chloroacetic acids between water and chloroform which were given in Section II (pp. 227, 228) of this paper are incorrect. The figures given represent the distribution between one volume of water and three volumes of chloroform. Correct figures for acetic acid were given in Section I (p. 215), $\mathfrak{P}$ (1000 M/L) = 0.25; $\mathfrak{P}$ (100 M/L) = 0.10. The data for chloroacetic acid are as follows:

	C_1	C_2	C_2/C_1	$\mathfrak{P}$
Chloroacetic acid	194.25	5.50	0.0283	*10*
(Chloroform)	199.00	5.50	0.0276	0.034
	86.50	1.6875	0.0195	
	68.25	1.250	0.0183	*1*
	42.75	0.625	0.0146	0.0168

[1] C_1 = concentration in water; C_2 = concentration in organic solvent. The italicized figures in the last column indicate the concentration in the organic solvent (C_2) to which interpolation is made to obtain $\mathfrak{P}$. Thus for chloroacetic acid, when C_2 = 10 M/L, $\mathfrak{P}$ = 0.034; and when C_2 = 1 M/L, $\mathfrak{P}$ = 0.0168.

The Partition Coefficients of the Acid between
Water and Ether, 25°

	C_1	C_2	C_2/C_1	[illegible]
Acetic acid[1]	1919.0	1026.0	0.535	
	1156.0	616.0	0.532	
	333.0	168.0	0.505	Mean
	73.3	416.0	0.568	0.535
Acetic acid	14.4	6.75	0.468	
	8.90	4.20	0.472	
	5.20	2.35	0.452	
	2.8625	1.2875	0.449	Mean
	1.075	0.475	0.442	0.456
Acetyl salicylic acid	1.32	8.84	6.7	*10*
	0.84	5.16	6.15	6.7
	0.49	2.75	5.62	
	0.31	1.57	5.06	*1*
	0.205	0.96	4.70	4.75
Anthranilic acid	6.04	6.80	1.125	
	3.57	4.04	1.130	
	1.86	2.21	1.190	
	0.100	1.05	1.050	Mean
	0.520	0.560	1.075	1.11
Benzilic acid	0.300	9.22	30.7	*10*
	0.160	4.44	27.7	31.8
	0.1200	2.72	22.65	
	0.0775	1.55	20.00	*1*
	0.0500	0.83	16.60	18.00
Benzoic acid	0.370	13.75	37.80	*10*
	0 270	8.130	30.15	33.0
	0.1575	4.8625	30.85	
	0.095	2.3850	25.15	
	0.065	1.6250	25.00	*1*
	0.0375	0.9125	24.30	25.00
Bromoacetic acid	4.25	9.55	2.245	*10*
	3.05	6.30	2.063	2.27
	1.475	3.475	1.760	
	1.3125	1.8875	1.438	*1*
	0.9625	1.3375	1.390	1.32

[1] Morgan and Benzon: Zeit. anorg. Chem., 55, 356 (1907).

	C_1	C_2	C_2/C_1	[illegible]
α-Bromopropionic acid	1.725	2.275	7.11	*10*
	1.30	9.50	7.30	7.4
	1.125	6.675	5.93	
	0.8625	4.8625	5.64	
	0.700	3.450	4.93	
	0.5875	2.7875	4.75	
	0.500	2.275	4.55	
	0.40875	1.68125	4.02	*1*
	0.3125	1.1250	3.60	3.48
Bromosuccinic acid	6.70	8.90	1.35	*10*
	3.50	3.85	1.10	1.38
	2.00	1.925	0.963	
	1.3625	1.1625	0.853	*1*
	0.63125	0.4500	0.712	0.84
n-Butyric acid	2.64	14.04	5.32	*10*
	1.80	9.20	5.12	5.2
	1.60	5.02	4.73	
	0.59	2.65	4.50	*1*
	0.335	1.40	4.18	4.05
s-Butyric acid	2.6	8.4	3.23	
	1.625	5.575	3.43	
	0.975	3.225	3.30	
	0.500	1.6125	3.22	Mean
	0.29375	0.85625	2.92	3.22
Chloroacetic acid	8.58	15.20	1.770	*10*
	7.80	13.40	1.718	1.58
	5.11	8.48	1.66	
	4.60	6.70	1.455	*1*
	2.85	3.70	1.299	1.020
	1.9375	2.3375	1.208	
	1.40	1.55	1.08	
o-Chlorobenzoic acid	1.360	9.68	26.80	*10*
	0.250	5.67	22.65	27.1
	0.1925	3.7075	19.30	
	0.145	2.415	16.65	*1*
	1.100	1.300	13.00	12.5
α-Crotonic acid	3.52	11.6	3.30	
	1.68	5.48	3.26	
	1.24	3.92	3.16	
	0.85	2.73	3.21	
	0.54	1.70	3.15	

	C_1	C_2	C_2/C_1	$\mathfrak{P}$
	0.52	1.60	3.08	Mean
	0.32	0.95	2.96	3.20
α-β-Dibromopropionic acid	0.450	3.2625	7.25	
	0.350	2.1000	6.00	
	0.25625	1.13125	4.42	*1*
	0.21875	0.85625	3.92	4.20
Dichloroacetic acid	9.5	25.9	2.72	*10*
	6.5	14.8	2.28	1.9
	4.05	6.95	1.72	
	2.325	2.675	1.15	*1*
	1.25	1.025	0.82	0.805
2.4-Dinitrobenzoic acid	2.495	7.78	3.12	*10*
	1.79	4.08	2.28	3.6
	1.45	2.51	1.73	
	1.15	1.69	1.41	*1*
	0.67	0.68	0.91	1.10
3.5-Dinitrobenzoic acid	0.365	6.395	17.5	*10*
	0.295	3.885	13.2	21.10
	0.225	2.655	11.8	
	0.1850	1.815	9.8	*1*
	0.1325	1.0475	7.9	7.7
Formic acid	30.00	13.25	0.442	*10*
	13.45	4.75	0.353	0.43
	8.85	3.25	0.368	
	6.55	2.30	0.351	
	4.775	1.625	0.340	0.320
Fumaric acid	8.85	6.75	0.763	
	4.80	3.50	0.729	
	2.60	1.70	0.654	
	1.5125	0.8375	0.554	*1*
	1.01875	0.4625	0.454	0.58
Gallic acid	59.5	27.0	0.453	
	35.2	16.10	0.457	
	22.0	10.00	0.454	
	15.75	7.13	0.452	
	8.25	3.72	0.452	Mean
	2.82	1.27	0.451	0.451
Gentisinic acid	1.12	11.92	10.65	*10*
	0.83	7.65	9.22	10.3
	0.60	3.98	6.64	
	0.41	2.07	5.05	*1*

	C_1	C_2	C_2/C_1	[illegible]
	0.31	1.205	3.89	3.6
Glutaric acid	11.90	3.65	0.306	
	6.40	1.875	0.292	
	3.0875	0.9125	0.296	
	1.300	0.34375	0.264	1
	0.70625	0.18750	0.268	0.296
Hippuric acid	8.04	2.80	0.348	
	4.66	1.70	0.364	
	2.58	0.98	0.380	
	1.42	0.56	0.394	1
	0.855	0.355	0.415	0.379
o-Iodobenzoic acid	0.1010	2.640	26.2	
	0.0602	1.400	23.2	
	0.0400	0.861	21.5	1
	0.0238	0.505	21.2	23.0
β-Iodopropionic acid	1.44	15.22	10.6	10
	0.900	8.66	9.6	10.0
	0.500	4.64	9.3	
	0.280	2.26	8.1	1
	0.175	1.275	7.3	7.3
Lactic acid	28.3	5.10	0.180	10
	15.7	2.70	0.172	0.191
	9.35	1.525	0.163	
	5.95	1.000	0.155	1
	3.95	0.550	0.139	0.155
Laevulinic acid	14.65	3.75	0.2575	
	10.10	2.65	0.2625	
	5.15	1.40	0.2725	
	2.57	0.725	0.2820	1
	1.725	0.500	0.2900	0.280
Maleic acid	11.45	1.90	0.166	
	7.25	1.025	0.141	
	4.85	0.75	0.153	
	2.50	0.35	0.140	1
	1.56	0.215	0.138	0.150
Malonic acid	94.60	14.0	0.148	
	34.42	5.17	0.150	
	22.30	3.44	0.154	
	7.90	1.05	0.133	
	3.80	0.5125	0.135	1
	2.1875	0.29375	0.134	0.134

	C_1	C_2	C_2/C_1	P
Mandelic acid	5.225	8.525	1.63	10
	3.225	4.825	1.495	1.66
	2.100	2.95	1.405	
	1.070	1.475	1.380	1
	0.885	1.175	1.330	1.30
m-Nitrobenzoic acid	0.240	6.812	28.8	10
	0.180	4.260	23.7	31.0
	0.135	2.905	21.5	
	0.095	1.875	19.7	1
	0.075	1.250	16.7	15.5
o-Nitrobenzoic acid	1.840	13.08	7.11	10
	1.200	6.96	5.80	7.1
	0.790	3.035	3.84	
	0.543	1.413	2.60	1
	0.379	0.663	1.75	2.17
Oxalic acid	84.25	9.60	0.113	10
	39.35	3.80	0.0965	0.116
	22.625	2.0375	0.0902	
	14.10	1.31	0.0930	1
	5.9375	0.525	0.0885	0.092
p-Oxybenzoic acid	1.4	12.8	9.15	10
	0.875	7.425	8.50	10.2
	0.575	5.025	8.72	
	0.400	3.250	8.13	1
	0.3125	2.2625	7.23	6.2
α-Oxybutyric acid	9.70	6.40	0.660	
	5.75	3.55	0.617	
	4.1375	2.7125	0.656	
	2.875	1.875	0.652	Mean
	1.7625	1.0875	0.617	0.633
β-Oxybutyric acid	6.60	2.36	0.356	
	4.75	1.70	0.358	
	3.05	1.075	0.352	
	1.725	0.600	0.348	Mean
	1.075	0.375	0.349	0.353
Phenylacetic acid	1.08	16.12	15.0	
	0.44	7.44	16.9	
	0.26	3.82	14.7	
	0.17	2.47	14.5	Mean
	0.085	1.255	14.7	15.2
Phthalic acid	6.675	6.575	0.985	10

	C_1	C_2	C_2/C_1	[illegible]
	3.800	3.375	0.888	1.04
	2.375	1.925	0.810	
	1.5375	1.100	0.716	*I*
	0.96875	0.66875	0.690	0.740
Propionic acid	5.45	8.30	1.52	
	2.35	3.375	1.435	
	0.925	1.225	1.325	*I*
	0.675	0.8875	1.315	1.32
Pyruvic acid	14.10	2.40	0.170	
	7.05	1.15	0.163	
	5.00	0.80	0.160	Mean
	3.65	0.55	0.151	0.162
Resorcinilic acid	0.50	12.75	25.50	*IO*
	0.3875	8.7125	22.50	23.0
	0.28125	4.51875	16.00	1
	0.1350	1.5950	11.81	9.4?
Salicylic acid	0.295	14.825	50.3	
	0.195	7.645	39.2	
	0.125	3.855	30.8	
	0.0850	2.415	28.4	*I*
	0.0666	1.3975	21.0	19.0
Succinic acid	13.8	2.75	0.199	
	7.95	1.55	0.195	
	4.3625	0.8625	0.1975	
	2.6250	0.4875	0.186	Mean
	1.6000	0.2880	0.180	0.192
Tartaric acid	98.75	6.0625	0.0613	
	37.56	2.5625	0.0683	
	21.62	1.50	0.0694	*I*
	8.40	0.625	0.0745	0.072
Thiacetic acid	9.70	8.5	0.877	
	6.00	5.3	0.884	
	3.175	2.675	0.843	
	1.39	1.165	0.839	*I*
	0.9675	0.8025	0.830	0.84
Trichloroacetic acid	8.825	17.00	1.928	*IO*
	6.640	10.62	1.600	1.50
	7.10	10.40	1.465	
	5.10	5.40	1.060	
	3.20	2.50	0.781	
	1.95	0.85	0.436	*I*

	C_1	C_2	C_2/C_1	[illegible]
	1.4625	0.5625	0.385	0.495
2.4.6-Trinitrobenzoic acid	8.28	5.88	0.710	*IO*
	4.80	2.20	0.458	0.88
	2.56	0.84	0.328	*I*
	1.09	0.200	0.182	0.36
Valeric acid	0.3900	5.6700	14.52	
	0.3000	4.3000	14.32	
	0.1700	2.2000	12.95	
	0.1125	1.4575	12.92	Mean
	0.0775	1.0225	13.20	13.54
iso-Valeric acid	1.325	11.0	8.32	
	0.8875	7.0875	7.98	
	0.5750	4.50	7.82	
	0.44375	3.275	7.70	*I*
	0.2500	1.875	7.50	7.04

Partition Coefficients of the
Amines between Water and Ether, 25°

Benzylamine	4.55	9.60	2.10	
	2.85	6.05	2.12	
	1.85	3.725	2.01	
	1.10	3.25	2.04	Mean
	0.675	1.335	1.97	2.00
Benzylethylamine	0.92	12.92	14.1	
	0.56	7.60	13.6	
	0.365	4.995	13.7	
	0.230	2.83	12.3	*I*
	0.145	1.74	12.0	11.6
Benzylmethylamine	2.08	12.84	6.17	
	1.14	5.66	5.84	
	0.645	3.665	5.69	
	0.41	2.12	5.17	*I*
	0.23	1.17	5.08	5.00
n-Butylamine	3.20	3.52	1.10	
	2.15	2.20	1.02	
	1.35	1.23	0.912	*I*
	0.85	0.76	0.895	0.905
iso-Amylamine	0.8375	1.8375	2.19	
	0.4875	1.0125	2.08	
	0.3750	0.6500	1.73	*I*
	0.2375	0.3875	1.63	2.02

	C_1	C_2	C_2/C_1	[illegible]
Coniine	1.06	7.38	6.95	
	0.62	3.72	7.16	
	0.33	1.875	5.68	
	0.19	1.055	5.55	6.33
Diethylamine	7.9	6,3	0.798	
	2.875	2.025	0.704	
	1.650	1.075	0.652	
	1.100	0.7375	0.671	*I*
	0.6125	0.4375	0.714	0.652
Dimethylamine	13.5	3.05	0.226	
	7.0	1.60	0.228	
	5.22	1.26	0.242	
	4.35	1.025	0.236	
	2.81	0.63	0.224	
	2.55	0.600	0.235	
	1.85	0.425	0.230	Mean
	1.37	0.33	0.241	0.231
Dipropylamine	1.48	9.76	6.6	
	0.92	5.70	6.2	
	0.60	2.97	4.95	
	0.43	1.915	4.46	*I*
	0.26	1.005	3.86	3.86
Ethylamine	14.8	2.50	0.169	
	9.8	1.60	0.163	
	6.075	1.125	0.185	
	3.975	0.675	0.170	Mean
	2.550	0.450	0.176	0.172
n-Heptylamine	0.385	8.00	20.8	
	0.275	5.145	18.7	
	0.200	3.105	15.5	*I*
	0.120	1.41	11.75	10.3
Methylamine	34.5	3.9	0.113	
	19.1	2.05	0.107	
	11.25	1.225	0.109	
	7.60	0.90	0.118	Mean
	4.90	0.575	0.117	0.113
n-Methylpiperidine	5.92	10.92	1.85	
	3.42	6.20	1.81	
	2.065	3.59	1.74	
	1.33	2.31	1.74	*I*
	0.805	1.37	1.70	1.68

	C_1	C_2	C_2/C_1	[illegible]
Piperidine	14.10	17.85	0.790	
	8.60	11.30	0.760	
	4.85	6.70	0.724	*I*
	2.60	3.80	0.685	0.655
	1.10	1.675	0.657	
Trimethylamine	6.30	8.90	0.707	
	3.00	4.45	0.675	
	1.775	2.65	0.670	
	1.1625	1.775	0.655	*I*
	0.800	1.2125	0.660	0.660

SOLUBILITIES AND COOLING CURVES OF THE MONO-NITROPHENOLS*

BY L. L. CARRICK

The first systematic theoretical work of note on solubility was done by van't Hoff;[1] who originally derived a solubility equation from the analogy between solutions and gases. He compared solubility to evaporation and saturation to maximum vapor pressure. Then starting with the fundamental thermodynamic equation

$$AVdP = \frac{q\,dT}{T} \qquad 1$$

he derived the solubility equation

$$\frac{d\log_e C}{dT} = \frac{Q}{AT\left(\frac{dP}{dC}\right)_T} \qquad 2$$

in which Q is defined as the heat absorbed in dissolving one mole of the solute in a saturated solution, the other terms having their usual meaning. Van Laar[2] has derived a somewhat similar equation connecting heat of solution and solubility in the case of electrolytes. The examples which he cites show close agreement between observed and calculated values. An equation showing another relation between solubility and heat of solution has been deduced from Planck's thermodynamic equation by Dahms.[3] Correct results were obtained in the two examples cited. Wilderman[4] and Colson[5] have also formulated equations showing relations between solubility and heat of solution, which like many others only record an interesting coincidence and are not capable of universal application.

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[1] van't Hoff Lectures, vol. 1, p. 35.

[2] Zeit. phys. Chem., **35**, 11–17 (1900).

[3] Wied. Ann., **64**, 507–518 (1898).

[4] Zeit. phys. Chem., **42**, 481–486 (1903).

[5] Comptes rendus, **162**, 753–56 (1916); **161**, 586–89; 787–90 (1915).

Solubilities calculated from conductivity measurements are in good agreement with the experimental values but the method has no general application, as it can only be used with advantage where the solute is sparingly soluble and is completely ionized in solution. It cannot be used at all for non-electrolytes.

Spencer[1] and Bodländer[2] have attempted to calculate the solubility of salts from electrode potentials. Good results were obtained by Spencer for $TlIO_3$. Bodländer's method gave results which varied greatly but were of the same magnitude. In many cases it was necessary to assume complexity of ions, or to make corrections for liquefaction and vapor pressure. In general there are special details to be observed, which entail a prior knowledge of a substance's solubility. Should the component be non-ionized the method is inapplicable.

Kyato[3] found a relation between indices of refraction and solubility and formulated an equation for calculating solubility which was later modified by Getman and Wilson.[4] The results of both formulae are only approximate, the largest error occurring in dilute solutions.

In the equation of Tyrer,[5] and Hardman and Partington[6] the solubility of a substance in any particular solvent is expressed as a function of the temperature. Hardman and Partington secured good results for the few solvents tested, but this would be true for a limited number of examples with almost any equation connecting temperature and solubility, which contains three constants depending on the nature of the solution.

Dolezalek[7] has assumed that the partial pressures of the constituents of an ideal mixture should be proportional

[1] Zeit. phys. Chem., **80**, 70–78.
[2] Ibid., **27**, 55 (1898).
[3] Mem. Coll. Sci. Eng., **1**, 265, 290–303 (1907).
[4] Am. Chem. Jour., **41**, 344–348 (1909).
[5] Jour. Chem. Soc., **97**, 1778–88 (1910).
[6] Ibid., **99**, 1769–75 (1911).
[7] Zeit. phys. Chem., **64**, 727 (1908); **71**, 191 (1910).

to the molecular concentration of each, and that the total pressure is the sum of the two linear partial pressures, the total pressure being then represented by a straight line. Out of 160 examples only 70 agreed with the theory while 90 were exceptions.

Starting from Gibbs'[1] function, Miller[2] has deduced a formula for the calculation of solubility, but he gives no examples of the application of his equation.

A formula analogous to that of Ramsay and Young[3] for the calculation of a complete vapor pressure curve from a knowledge of the vapor pressure of a substance at two temperatures and a complete vapor pressure curve for another substance is proposed by Findlay.[4] He proposes the equation

$$R = R' + C(t' - t) \qquad\qquad 3$$

in which R and R′ are the ratios of the absolute temperatures at which the substances have the same solubilities. C is a constant with a small positive or negative value and is different for each solubility curve; t' and t are the two temperatures at which one of the substances has the two values of the solubility in question. The calculated results from this equation are quite good as long as the curves are regular.

J. H. Hildebrand[5] has approached the subject of solubility from the standpoint that Raoult's law is more applicable to solutions than van't Hoff's equation, as most investigators heretofore have held. With this in mind he has derived the expression

$$\log N = -\frac{L(T_m - T)}{4.58\,TT_m} \qquad\qquad 4$$

in which N is the solubility in mole fractions, L the molecular heat of fusion of the solute, T_m the melting point on the absolute scale of the pure solute and T the absolute temperature

[1] Trans. Conn. Acad. iii (1876–1878).
[2] Jour. Phys. Chem., **1**, 633–642, 1896–97.
[3] Phil. Mag., (V) **21**, 33, 1886.
[4] Proc. Roy. Soc., **69**, 471–78 (1902).
[5] Jour. Am. Chem. Soc., **38**, 1452–73 (1916); **39**, 2297–2301 (1917); **41**, 1067–80 (1919).

at which the solubility is desired. Hildebrand states that positive variations are to be expected when the internal pressure of the solute and solvent are not the same, and when the solute and solvent are polar, that is they tend to form compounds with each other. Since no account is taken of the variation of the heat of fusion with the temperature the solubility curve constructed by plotting solubility in mole fractions as abscissas and temperature as ordinates is approximately a straight line.

Schröder,[1] Le Chatelier[2] and van Laar[3] have derived the equation

$$d \log_e x = \frac{L\,dT}{RT^2} \qquad \text{.......................5}$$

which when integrated gives the equation

$$\log_e x = -\frac{L\,(T_o - T)}{R\,T_oT} \qquad \text{.............6}$$

in which x is the mole fraction of the solvent, R the gas constant, L the latent heat of fusion of the pure solvent, T_0 the absolute temperature of fusion of the pure solvent and T the absolute temperature at which the solvent melts in the presence of the second component.

Baud and Gay[4] have derived the same expression starting from the Clapeyron equation

$$LdT = AT(V - U)dP \qquad \text{................7}$$

Washburn[5] has also deduced this same equation by combining the equation of Boldingh

$$\pi = -\frac{\log_e x\ RT}{V_o} \qquad \text{.......................8}$$

representing the relation between osmotic pressure and concentration of the solution, with the equation connecting osmotic pressure and freezing point

[1] Zeit. phys. Chem., **11**, 449 (1893).
[2] Comptes rendus, **118**, 638 (1894).
[3] Proc. Akad. Wet. Amsterdam, **5**, 424; **6**, 21 (1903).
[4] Comptes rendus, **150**, 1687(1910).
[5] "Principles of Physical Chemistry," p. 172.

$$\frac{d\pi}{dT} = -\frac{L}{V_0T} \quad \text{.........................} 9$$

so as to eliminate $d\pi$, the osmotic pressure.

If we express the solubility of the solvent in terms of the mole fraction of a saturated solution it is claimed that the solvent, when associated with any solute to form an ideal solution, is entirely independent of the nature of the solute. This is on the assumption that there is no dissociation or association. Substances which are either, do not fall under the category of ideal solutions and consequently the equation does not express the relationship between them. Under the above assumption solubility is a function of the temperature only.

Both Washburn, and Baud and Gay have tested Equation 6 for binary mixtures which are ideal solutions, and found that it gives excellent results compared with the experimental values. This equation as been verified by the writer in the case of mixtures of the mono-nitrophenols.

Experimental

Purification of Materials.—Acetone: C. P. acetone after standing in contact with quick-lime for two days, with frequent shaking, was distilled. The fraction passing at 56.3 deg. C was retained and fractionated over anhydrous copper sulphate. Only the fraction passing at 56.3 deg. C (corrected) was collected and set aside for use. When tested for impurities[1] no test for residue, acids, aldehydes, water, substances oxidizable by permanganate was obtained. It was miscible with an equal volume of water yielding a clear solution.

Benzene: C. P. benzene was twice distilled over anhydrous copper suplhate. A four-bulb fractionating column was used. Only the fraction passing at 80.36 deg. C (corrected) was retained. The presence of water, carbon disulphide and thiophene was not detected.

[1] Outline of the tests used for impurities will be found in "Chemical Reagents, Their Purity and Tests" by E. Merck.

Ethyl alcohol: This was purified by allowing to stand two days in contact with quick-lime, with frequent agitation. The supernatant liquid was decanted and distilled over fresh quick-lime. The fraction passing at 78.4 deg. was collected. To insure dehydration and the removal of impurites with lower boiling points it was again distilled. A fractionating column and anhydrous copper sulphate were employed, and again only the fraction retained that distilled sharply at 78.4 deg. C (corrected). It gave no test for residue, fusel oil, molasses, alcohol, aldehydes, acetone or organic matter.

Ethyl ether: U. S. P. ethyl ether was shaken with distilled water four times to remove any traces of alcohol and twice distilled over fused calcium chloride. Each time it was distilled, only the fraction boiling at 35 deg. C was retained. It was distilled a third time with the aid of a fractionating column and anhydrous copper sulphate, the fraction passing sharply at 35 deg. C (corrected) was collected for use. No residue, aldehyde, water or acetone was detected.

Ortho- and para-nitrophenol: The para-nitrophenol was crystallized several times from water. The final product melted at 114 deg. C (corrected), the accepted melting point. The ortho-nitrophenol was first steam distilled and then crystallized from alcohol. It melted at 44 deg. C.

Meta-nitrophenol:[1] The meta-nitrophenol was prepared from meta-nitroaniline by diazotizing with potassium nitrite and boiling the diazonium compound until the evolution of nitrogen ceased. On extraction with ether it was found that any tar resulting from the diazotization was also taken up by the ether. The ether was distilled off, and the tar and meta-nitrophenol were separated by heating with (1:1) dilute sulphuric acid. The tar floated on the surface of the dilute acid and the meta-nitrophenol crystallized out. The meta-nitrophenol was recrystallized from water until a product melting at 93 deg. C (corrected) was obtained, which remained unaltered on further crystallization.

[1] The meta-nitrophenol was prepared in the laboratory of the North Dakota Agricultural College.

Method of Determining Solubility.—A method similar to the one herein described, but differing in some particulars, was used by N. V. Sidgwick[1] for the solubility determinations of the mono-nitrophenols in water. The method which the writer has used will be described in some detail, as it seems to be one which may be used to advantage in the determination of the solubility of solid substances whose equilibrium in solution is quickly attained.

Some of the material whose solubility is desired, is weighed into a 50 to 75 cc ground-glass-stoppered erlenmeyer flask of known weight. The amount of solute should be sufficient to saturate the solvent at 0 deg. C, when the solvent fills the flask about two-thirds full. A little solvent is added to the solute in the flask, the exact amount being determined after the saturation point has been determined by weighing the flask and contents. Only enough solvent should be added to produce a saturated solution of the substance near the boiling point of the solvent. After the addition of the solvent, the flask, with stopper removed, is immersed to within an inch of the top in a two liter beaker filled with distilled water. The water in the beaker is agitated mechanically and the flask is agitated continuously to hasten equilibrium between solute and solvent. The bath is heated with an electric hot plate provided with a variable resistance. The temperature is determined by a recalibrated thermometer suspended in the bath to the same depth as the solution in the flask. The temperature of the bath is gradually raised until the last crystals have gone into solution, this temperature being noted. The flask is removed and both the flask and bath cooled slightly below the saturation point. Then the flask is replaced in the bath and the temperature raised very slowly, the approximate temperature being already known. Just before the last crystals have gone into solution the glass stopper is inserted. The point at which the last crystal dissolves is read accurately, this point being the saturation temperature. The flask is now removed, cooled to room temperature, dried and weighed. The difference between this weight and the weight of the

[1] Jour. Chem Soc., 107, 1202–1213 (1915).

flask after the addition of the solute is the amount of solvent required to form a saturated solution with the given amount of solute at the temperature at which the last crystal went into solution. To find the next point on the curve, it is only necessary to add a little more solvent and repeat the above operation for saturation temperature. This time only one weighing is required to determine the amount of solvent used, while the amount of solute is the same as for the preceding point.

By this method it is quite often possible to determine an entire saturation curve in the time usually required, by other methods, to locate one point. The solubility is determined under atmospheric pressure. The solvent which escapes before saturation does not vitiate the results. The solute, however, must be nonvolatile at the working temperature. Errors due to analytical methods and manipulation are avoided. It must be borne in mind as pointed out above, that the method is of value only when equilibrium between solvent and solute is quickly attained.

This was the method used in determining the solubility of each of the mono-nitrophenols in acetone, benzene, ethyl alcohol, and ethyl ether. The results are tabulated in Tables I, II, III, and IV.

TABLE I

Solubility in acetone of

Ortho-nitrophenol			Meta-nitrophenol			Para-nitrophenol		
Temp. of satura-tion, °C.	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution
36.5	1236.67	92.56	84.0	1305.88	92.88	97.0	1192.50	92.30
30.3	566.29	84.98	74.5	905.20	90.05	85.6	791.31	88.78
26.1	398.97	79.97	63.0	533.20	84.21	75.2	546.81	84.54
20.1	258.96	70.50	55.2	422.81	80.87	61.7	408.86	80.16
16.1	211.37	67.88	43.0	301.32	75.08	50.4	327.92	76.63
11.5	166.48	62.48	34.5	255.22	71.85	41.2	284.10	73.97
6.0	131.42	56.79	25.0	223.43	69.08	33.2	262.74	72.43
+0.2	102.44	50.60	10.1	190.91	65.63	24.6	229.80	69.66
—	—	—	+0.2	169.35	62.95	18.1	221.23	68.87
—	—	—	—	—	—	10.1	204.47	67.15
—	—	—	—	—	—	0.0	188.28	66.99

TABLE II

Solubility in benzene of

Ortho-nitrophenol			Meta-nitrophenol			Para-nitrophenol		
Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution
40.1	873.57	89.73	87.8*	852.51	89.55	104.2*	1071.96	91.54
34.6	561.59	84.88	85.0	571.09	84.98	96.5*	400.02	80.00
30.1	365.41	78.51	81.5	375.51	79.05	91.0*	124.54	56.05
26.9	246.49	72.79	74.0	120.43	54.63	85.4	61.71	38.09
20.1	148.30	59.72	66.0	45.94	31.48	78.5	25.18	20.11
14.1	103.84	50.94	57.5	20.96	17.37	73.5	15.99	13.78
6.0	68.11	40.51	48.0	9.86	9.18	65.5	8.79	8.08
0.0	45.89	31.45	38.0	4.99	4.75	59.4	5.35	5.08
—	—	—	22.0	1.83	1.79	41.3	2.83	2.75
—	—	—	6.0	.63	.62	32.1	1.67	1.63
—	—	—	—	—	—	20.1	.96	.95
—	—	—	—	—	—	8.0	.65	.64

TABLE III

Solubility in ethyl alcohol of

Ortho-nitrophenol			Meta-nitrophenol			Para-nitrophenol		
Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of satura-tion, °C	Gm solute in 100 gm solvent	Gm solute in 100 mg solution
41.3	1038.44	91.22	85.0	1105.25	91.72	89.8	1016.75	91.05
37.3	545.48	86.68	77.2	851.47	89.49	81.1	800.35	88.89
34.3	200.09	66.67	65.5	554.25	84.71	71.2	545.00	84.50
30.2	69.58	41.03	57.5	422.62	80.87	62.7	415.55	80.60
23.1	34.31	25.54	50.7	345.27	77.54	52.7	319.52	76.16
17.3	22.08	18.09	45.5	301.54	75.20	45.2	278.94	73.61
12.4	17.71	15.04	30.5	221.24	69.03	38.6	244.89	71.01
6.7	13.00	11.50	23.4	183.77	64.75	26.1	193.78	65.96
0.0	10.16	9.22	11.0	143.55	58.94	18.5	161.13	61.70
—	—	—	+1.0	116.91	53.87	10.0	133.84	57.23
—	—	—	—	—	—	0.0	115.75	53.65

* Solubility determined in a sealed tube.

TABLE IV
Solubility in ethyl ether of

Ortho-nitrophenol			Meta-nitrophenol			Para-nitrophenol		
Temp. of saturation, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of saturation, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution	Temp. of saturation, °C	Gm solute in 100 gm solvent	Gm solute in 100 gm solution
37.5	915.85	90.23	83.0	1065.84	91.42	101.9*	1001.50	90.92
33.2	480.61	82.79	75.0	508.89	83.58	97.1*	586.58	85.51
27.8	249.45	71.38	68.0	355.06	78.03	87.8*	380.29	79.23
21.9	138.79	58.12	59.0	269.22	72.92	70.5	249.39	71.38
15.8	81.07	44.75	48.5	212.75	68.02	59.9	202.07	66.89
10.5	59.41	37.27	39.5	178.74	63.89	46.8	167.66	62.64
5.5	44.81	30.95	23.5	143.67	58.96	38.1	149.29	59.89
1.0	37.76	27.41	12.2	127.24	55.99	31.7	139.23	58.20
—	—	—	8.2	118.20	54.17	28.7	133.02	57.07
—	—	—	+0.2	105.92	51.44	24.1	131.18	56.74
—	—	—	—	—	—	18.0	122.95	55.06
—	—	—	—	—	—	10.1	115.56	53.61
—	—	—	—	—	—	1.0	109.99	52.38

The results of Tables I, II, III, and IV are depicted graphically in Figs. 1, 2, 3, and 4.

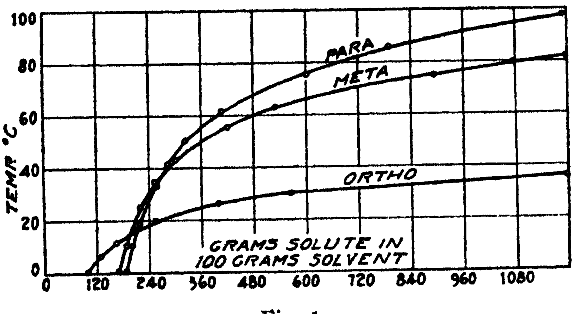

Fig. 1
Solubility of the Mono-nitrophenols in Acetone

Although the literature contains many references concerning the solubility of the mono-nitrophenols in the four solvents used, there seems to be but one quantitative reference. Bogojawlenski[1] has recorded the solubility of these isomers

* Solubility determined in a sealed tube.
[1] Schrift. Dorpat. Naturforsch-Ges., **15**, 216–29 (1907).

in benzene and that of the ortho- and para-nitrophenol in water. On comparing his results for the solvent water with those of Sidgwick,[1] I find that there exists the same divergence as between the results obtained by me for benzene and those of Bogojawlenski.

From Fig. 2 it will be seen that benzene is a good extraction solvent to use in extracting ortho-nitrophenol from either or both of its two isomers. Thus at 40 deg. C 100 grams of benzene will dissolve 850 grams of the ortho-nitrophenol while it will dissolve less than 10 grams of either of

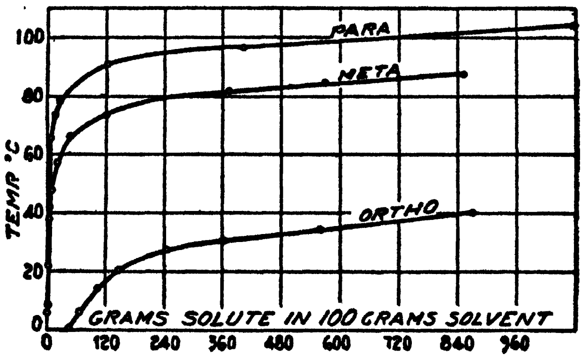

Fig. 2

Solubility of the Mono-nitrophenols in Benzene

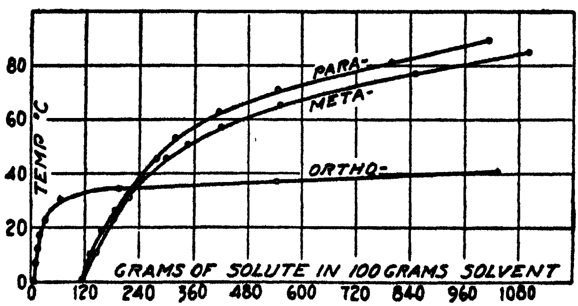

Fig. 3

Solubility of the Mono-nitrophenols in Ethyl Alcohol

[1] Jour. Chem. Soc., 107, 1202–1213 (1915).

the other two isomers. Fig. 3 shows that ethyl alcohol should be a good solvent for the purification of the ortho-nitrophenol by crystallization. The solubilities of the mononitrophenols in acetone and ethyl ether lie too close together for any practical application. None of these solvents are suitable for the separation of the meta- and para- forms.

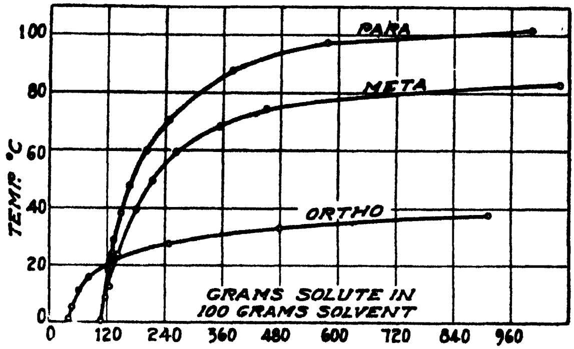

Fig. 4
Solubility of the Mono-nitrophenols in Ethyl Ether

Carnelley and Thompson[1] have formulated the following rules to enable one to predict the solubility of organic isomers: (1) For any series of isomeric organic compounds the order of solubility is the same as the order of fusibility, i. e., the most fusible compound is likewise the most soluble. (2) For any series of isomeric compounds the order of solubility is the same no matter what may be the nature of the solvent. (3) The ration of the solubility of any two isomers in any given solvent is very nearly constant and is therefore independent of the nature of the solvent.

The first rule holds for the solubility of these isomers in benzene, but it does not hold for any one of the other three solvents. In fact the order of solubility of the three isomers does not remain the same for different temperatures in the same solvent. Thus with acetone as solvent the order of solubility at 5 deg. C is ortho-, meta- and para-, the para-being the most soluble and the ortho- the least soluble, while

[1] Jour. Chem. Soc., **53**, 782–805 (1883).

at 20 deg. C the ortho- is the most soluble and at 50 deg. C the para- is the least soluble. Thus the order at the higher temperatures is completely the reverse of the order at the lower temperatures. The second rule does not hold. We have four solvents and there are three different orders of solubility, except near the point where the ortho- is miscible in all proportions with a small amount of solvent. The third rule is not even an approximation for the solubilities herein recorded, for in three of the four figures the solubility curve for the ortho- crosses the curve for the other two substances which would preclude any possibility of there being a nearly constant ratio between the solubility of the ortho- and that of either of the other two substances. Thus for the solubility of the isomeric mono-nitrophenols in the four solvents used the generalizations of Carnelley and Thompson are of no value in predicting their solubilities.

The writer has attempted to calculate the solubility of these solutes in the different solvents, by the various equations referred to in the introduction, but in no case was there more than approximate agreement. The equations of Findlay and Hildebrand were found by the writer to give the best results. The solubilities calculated by Equation 4 in acetone and the observed values for the ortho-, meta- and para-nitrophenols in actone are given in Table V. In Table VI appears only the calculated values for the ortho- and para-nitrophenols as the meta-nitrophenol curve was used as a curve of reference.

The data incorporated in Table V is depicted graphically in Figures 5, 6 and 7, together with the observed curves for each solute in the other three solvents employed. The graphic representation of the data in Table VI is shown in Figure 8.

In applying Equation 3 the writer selected the meta-curve as a curve of reference as it bears a closer relation to both the para- and ortho- curves than either the para- or the ortho-curve does to the other two isomeric curves. By reference to Figures 1, 2, 3, and 4 it is manifest that the solubility curves of the isomeric mono-nitrophenols in acetone are as uniform throughout their entire length as any other solvent investigated.

TABLE V

Comparison of solubility in acetone as observed and calculated by Equation 4

Ortho-nitrophenol			Meta-nitrophenol			Para-nitrophenol		
Temp. of saturation, °C	Solubility in mole fractions		Temp. of saturation, °C	Solubility in mole fractions		Temp. of saturation, °C	Solubility in mole fractions	
	Obs.	Calc.		Obs.	Calc.		Obs.	Calc.
36.5	.835	.866	84.0	.845	.864	97.0	.869	.790
30.3	.702	.767	74.5	.791	.735	85.6	.767	.666
26.1	.624	.702	63.0	.691	.597	75.2	.695	.565
20.1	.519	.618	55.2	.638	.514	61.7	.629	.449
16.1	.471	.565	43.0	.557	.400	50.4	.577	.365
11.5	.410	.508	34.5	.516	.333	41.2	.543	.305
6.0	.353	.447	25.0	.481	.267	33.2	.522	.258
+0.2	.300	.388	10.1	.444	.191	24.6	.489	.215
—	—	—	+0.2	.415	.140	18.1	.482	.185
—	—	—	—	—	—	10.1	.460	.155
—	—	—	—	—	—	0.0	.437	.117

TABLE VI

Comparison of solubility in acetone as observed and calculated by Equation 3

Ortho-nitrophenol C = —0.00268					Para-nitrophenol C = 0.000472				
Temperature of saturation, °C			Solubility in mole fractions		Temperature of saturation, °C			Solubility in mole fractions	
Observed meta-	Calculated ortho-	Observed ortho-	Observed ortho-	Calculated ortho-	Observed meta-	Calculated para-	Observed para-	Observed para-	Calculated para-
0.0	12.2	12.1	.415	.410	0.0	—5.2	—	—	—
5.0	13.3	13.2	.432	.427	10.1	—	2.3	.442	.425
10.0	14.5	14.2	.443	.435	20.0	17.6	11.1	.460	.445
16.0	—	15.8	.463	.453	30.0	28.4	26.4	.500	.493
20.0	16.8	16.6	.475	.468	41.2	—	42.0	.550	.555
30.0	19.1	19.1	.507	.507	50.0	51.1	54.1	.597	.608
40.0	21.1	22.0	.552	.567	60.0	63.0	67.0	.654	.678
44.0	—	—	—	—	70.0	74.8	80.0	.727	.767
50.0	23.1	24.5	.592	.640	80.0	86.4	92.3	.817	.893
60.0	24.8	25.2	.608	.668	90.0	—	—	—	—
70.0	26.5	31.2	.725	—	—	—	—	—	—

Hence, Equation 3 when applied to the calculation of the solubility of the mono-nitrophenols in acetone gives as good results as in any of the other solvents used. Even so the solubilities calculated by Equation 3 only approximate the observed values. The agreement given is much closer than it otherwise would be if I had not assumed the point of intersection as one temperature in the calculations. Results that agree fully as well could have been obtained if any point on the curve and the fusion temperature of the pure solute had been used. The relation is only approximate and unless you know the point of intersection of the curves, if there is one, it is still more approximate.

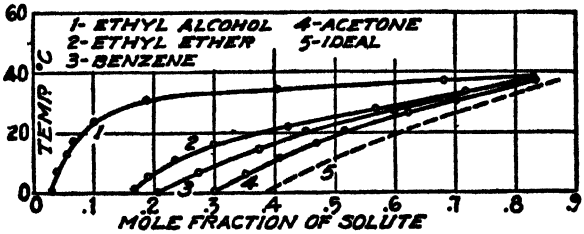

Fig. 5

Comparison of the Ideal Solubility Curve of o-Nitrophenol, calculated by Equation 4, with its Solubility Curves in Acetone, Benzene, Ethyl Alcohol, and Ethyl Ether

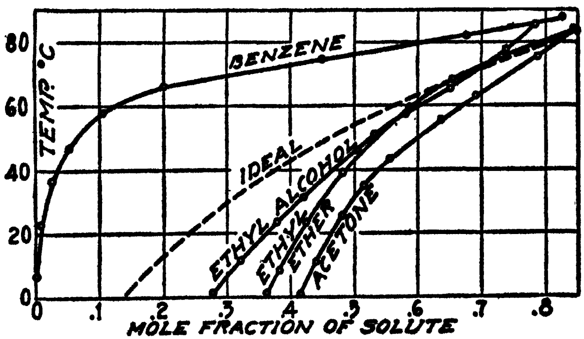

Fig. 6

Comparison of the Ideal Solubility Curve of m-Nitrophenol, calculated by Equation 4, with its Solubility Curves in Acetone, Benzene, Ethyl Alcohol, and Ethyl Ether

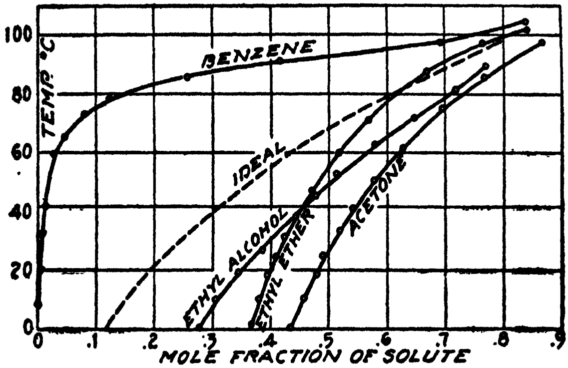

Fig. 7
Comparison of the Ideal Solubility Curve of p-Nitrophenol, calculated by Equation 4, with its Solubility Curve in Acetone, Benzene, Ethyl Alcohol, and Ethyl Ether

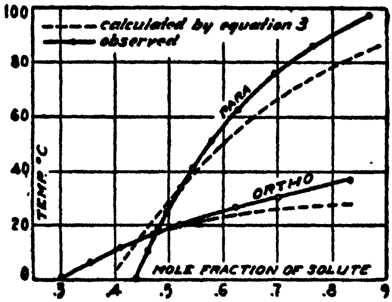

Fig. 8
Comparison of the Observed Solubility in Acetone of o-, p-Nitrophenol with that calculated by Equation 3

The variation in the calculated solubilities, Table V, would be explained by Hildebrand on the basis that these substances do not form ideal solutions, therefore do not follow Raoult's law. As pointed out by Hildebrand[1] when there is a great difference between the internal pressures of the solute and solvent or when the substances are polar, there will be a positive deviation of both components from Raoult's law. In Table VII is shown the relation between the internal pressures of these substances at 20 deg. C.

[1] Jour. Am. Chem. Soc., 41, 1067–80 (1919).

TABLE VII

Internal pressures at 20 °C

	Surface tension γ *	Boiling point t_b	van der Waals' a..10⁴	Molecular volume V	Internal pressures calculated from: Surface tension $\gamma/\sqrt[3]{V}$	Heat of vaporization $\frac{5200 + 30t_b}{V}$	Critical data $\frac{a}{V^2} \cdot 10^5$
Ethyl ether[1]	17.1	34.6	346	103.8	3.64	60.1	3.20
Acetone	23.5	56.3	246 #	73.3	5.85	94.0	4.58
Benzene[1]	28.9	80.0	373	88.8	6.48	85.6	4.72
Ethyl alcohol	21.7	78.4	240 #	57.6	5.61	129.7	7.09
o-Nitrophenol	40.7	214	801[2]	104.5[3]	8.64	111.2	7.34
m-Nitrophenol	45.0	194 @ 70mm	801[2]	102.0[4]	9.63	—	7.70
p-Nitrophenol	52.4	—	801[2]	101.5[3]	11.23	—	7.78

The internal pressures have been arranged in ascending order in the last column of Table VII. The other two methods of calculating the internal pressures do not give results that retain the same order. This may be due to incorrect assumptions either in the method of calculation or the data at hand. None of the internal pressures are the same, but as we shall see from the latter part of this paper the mono-nitrophenols dissolve one in the other according to Raoult's law, even though their internal pressures are not the same. We should expect, then, from internal pressure measurements that ethyl alcohol would be a good solvent to test Equation 4, but it does not give results that are any more comparable to the observed than does acetone.

From Figures 5, 6, and 7 we see that the solubility curves of ortho-nitrophenol in the four solvents used come nearer

[1] Jour. Am. Chem. Soc., **41**, 1067(1919).
[2] Jour. Chim. phys., **14**, 3 (1916).
[3] Liebig's Ann., **223**, 263 (1884). The density was calculated in the undercooled condition from the relation given by Schiff thus:

o-nitrophenol $t^0 = 1.2945 - 0.001385(t - 45.2) - 0.0000295(t - 45.2)$

p-nitrophenol $t^0 = 1.2809 - 0.00095(t - 114)$

[4] Only an approximate value.
* Jour. Am. Chem. Soc., **39**, 541–96 (1917).
\# "Recueil de Constants Physiques," p. 244.

to conforming to the ideal solubility curve than do those of the meta or para- form. This is what we are led to expect for the internal pressure of the ortho- form and those of the solvents are closer together than in the case of these solvents and the meta- and para- forms, but we have no criterion to explain the marked deviation of ortho-nitrophenol in ethyl alcohol. It should according to internal pressure measurements agree closer than any of the other solvents. This might be attributed to dissociation, association or the formation of compounds between the solute and solvent. Even if one of these conditions does prevail it only explains the deviation of the observed and calculated curves, it does not explain why ortho-nitrophenol, which is almost normal in benzene[1] and has a greater difference in internal pressure, lies closer to the ideal curve, or for that matter why any of the other solvents lie between it and the ideal curve.

Benzene when employed as a solvent for the isomeric mono-nitrophenols does not comply to Raoult's law, even though it is not itself associated or dissociated. Auwers[1] gives the association factor for para- in benzene as 1.38 and that of ortho- as almost normal. This would explain the deviation of the para- form but leave the explanation of the ortho- unsettled.

None of the methods of calculating solubility proposed to date are applicable to more than a small range of conditions and a small number of substances. In order to know which expression will apply we are compelled to determine experimentally the solubility.

Method of Determining the Melting Points of Binary Mixtures

The sample has in each instance been heated to above the melting point and under slow cooling the freezing points have been determined. As the temperature at which crystallization begins, may vary greatly, the true freezing point, due to undercooling, is not necessarily the temperature at which

[1] Zeit. phys. Chem., 12, 689 (1893).

the first crystals appear. Cooling curves for each different mole fraction of solvent have been determined. In all the cooling curves a decided arrest at the maximum temperature of crystallization was noted, which continued for an interval of one to two minutes, followed by a rapid fall in temperature. This temperature was taken as the correct freezing point. If there had been no marked arrest, as there was in a limited number of cases, and the cooling curve had been gradual and regular it would have been necessary to have taken the intersection of the cooling curve of the liquid and the cooling curve of the solvent, projected, as the correct freezing point. The readings were taken at half-minute intervals for the freezing point of the pure solvent.

After the arrest due to the crystallization of the pure solvent the mixture was cooled until it became rigid. In most instances, see Tables VIII, IX and X, a second arrest was observed. This was the separation of the eutectic mixture. Even though the observation of a second arrest was prevented by the mass becoming too rigid to stir, at a temperature above the eutectic temperature, a liquid phase could be seen between the crystals.

The apparatus consisted of a test-tube containing the sample, a looped glass stirrer and a thermometer graduated to 0.1 deg. C. This thermometer as well as all others used was recalibrated. The test-tube was surrounded by a larger tube which was placed in a water bath, heated by the free flame of a bunsen burner. The bath was maintained at about 5 deg. C below the temperature of the cooling mixture. The water bath was agitated mechanically and the mixture stirred by hand. This was especially necessary in determining the eutectic arrest. The mixture at this stage usually became so thick a mechanical stirrer failed to produce proper mixing of the components.

By this method the melting points of the three binary systems of the mono-nitrophenols were determined. The freezing point temperatures for the mixtures are given to the nearest 0.1 deg. C corrected for the immergent stem of the

thermometer. The composition of the mixture is given in mole fractions. Since the substances are isomers the mole and weight percent are the same and either may be found by multiplying the mole fraction by 100.

The calculated values were calculated by Equation 6. In using this equation it is necessary to know the variation of Q with the temperature, Q being the latent heat of fusion. As the literature does not give the specific heats of the mono-nitrophenols in the solid and liquid state, except for solid o-nitrophenol, and since the specific heats of other organic compounds have been found to remain fairly constant, the writer has assumed that the change in specific heat with change in temperature is small and hence the variation of the latent heat of fusion of the mono-nitrophenols remains nearly constant. The total variation is usually small in comparison to the latent heat of fusion at the melting point of the pure substance. It may be neglected without much error. Q is thus assumed to remain constant throughout the range of temperature employed. Bruner[1] gives the molecular heat of fusion of o-nitrophenol as 3725 cal. Substituting this value in Equation 6 and putting $T_0 = 317$ deg. A., the melting point of pure o-nitrophenol, we have the equation

$$T = \frac{815}{2.571 - \log_{10}x} \quad \ldots\ldots\ldots\ldots\ldots 10$$

in which T is the resulting melting point after the addition of para- or meta-nitrophenol, and x is the mole fraction of the ortho- component. This is the equation employed in calculating the freezing points of the mixtures in Tables VIII and IX, for the left branch, in which o-nitrophenol was considered as the solvent.

The observed and calculated values for the binary system o-nitrophenol and para-nitrophenol are given in Table VIII.

The results of Table VIII are plotted in Figure 9.

[1] Ber. deutsch. chem. Ges., **27**, 2106 (1894).

TABLE VIII
The binary system: o-nitrophenol, p-nitrophenol

Mole fraction of		Freezing point °C			
o-Nitrophenol	p-Nitrophenol	Solvent Obs.	Solvent Calc.	Eutectic observed	Solid phase
1.000	.000	44	—	—	
.909	.091	40.2	39.1	—	
.833	.167	37.5	34.5	34.6	First arrest o-nitrophenol, second eutectic
.800	.200	36.5	32.5	34.6	
.770	.230	34.7	30.6	34.6	
.750	.250	34.7	31.8	34.7	Eutectic
.730	.270	35.9	35.4	34.5	
.667	.333	44.5	45.7	34.7	
.625	.375	51.4	53.1	34.5	
.588	.412	56.7	57.1	34.5	
.555	.445	61.3	—	34.5	
.500	.500	67.5	68.0	34.2	First p-nitrophenol, second eutectic
.444	.556	73.6	75.3	34.4	
.375	.625	80.3	81.6	34.5	
.333	.667	84.1	85.8	34.4	
.286	.714	89.0	90.2	—	
.231	.769	94.0	95.2	—	
.161	.833	99.7	100.8	—	
.091	.909	106.0	106.9	—	
.000	1.000	114.0	—	—	

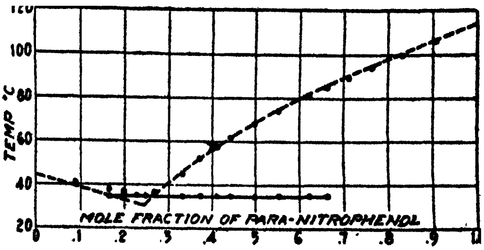

Fig. 9
Cooling Curve of the Binary Mixture: o-, p-Nitrophenol, calculated by Equation 6

The eutectic point is at 34.5 deg. C corresponding (by extrapolation) to 27% of p-nitrophenol. The calculated and observed values agree very well, although from internal pressure measurements we would not expect such good agreement.

The results for the binary system o-nitrophenol, m-nitrophenol are given in Table IX. In computing the calculated values the same equation was used as for Table VIII, for the left branch of the curve in which ortho- is the solvent, but Equation 12 was used for the right branch in which meta- was the solvent.

TABLE IX

The binary system: o-nitrophenol, m-nitrophenol

Mole fractions of		Freezing point °C			
o-Nitrophenol	m-Nitrophenol	Solvent Obs	Solvent Calc.	Eutectic observed	Solid phase
.000	1.000	93	—	—	
.091	.909	88.8	87.1	—	First arrest m-nitrophenol, second eutectic
.167	.833	83.9	81.8	—	
.231	.769	79.2	77.1	—	
.286	.714	75.4	73.3	—	
.333	.667	72.3	69.1	31.5	
.375	.625	68.6	65.5	31.5	
.412	.588	65.1	62.3	—	
.445	.555	62.7	59.3	31.6	
.500	.500	57.1	53.9	—	
.527	.473	54.2	51.1	31.5	
.555	.445	50.2	48.2	—	
.588	.412	46.8	44.4	31.7	
.625	.375	40.4	40.0	31.5	
.666	.334	35.2	34.7	31.5	
.714	.286	31.6	28.0	31.5	
.769	—	—	—	—	Eutectic
.833	.231	33.5	30.6	—	First arrest o-nitrophenol, second eutectic
.909	.167	35.9	34.6	31.5	
1.000	—	—	—	31.5	
—	.091	39.1	39.1	—	
—	.000	44	—	—	

The results of Table IX are plotted in Figure 10.

The eutectic is at 31.5 deg. C corresponding (by extrapolation) to 70% of o-nitrophenol. Here as in the previous figure the observed agrees very well with the calculated values.

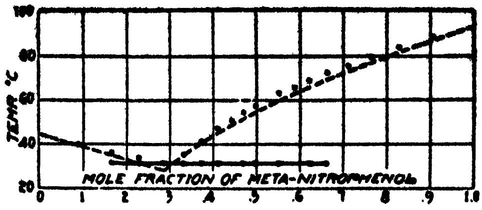

Fig. 10
Cooling Curve of the Binary Mixture: o-, m-Nitrophenol, calculated by Equation 6

In Table X are given the results for the binary mixtures m-nitrophenol, p-nitrophenol. Since the literature does not give the value of Q in the case of p-nitrophenol, the writer has taken a point on the curve of Figure 9 and calculated the heat of fusion. Thus for p-nitrophenol, taking the point where $x = 0.445$ and $T = 334.3$ deg. A and substituting in Equation 6, putting $T_0 = 387$ deg. A, we find

$$Q = 3950 \text{ cal. per mole.}$$

Assuming this value for Q to remain constant and putting $T_0 = 387$ deg. A in Equation 6, we find

$$T = \frac{864.3}{2\ 2331 - \log_{10}x} \qquad\qquad 11$$

which is the Equation I have employed in calculating the results in Table X for the branch of the curve in which para- is the solvent. Since in Table VIII we consider the p-nitrophenol the solvent as well as the o-nitrophenol, this equation was applied in the calculation of the results for Table VIII in the right branch of the curve where para- is the solvent.

The results of Table X are plotted in Figure 11.

The eutectic is at 61 deg. C corresponding (by extrapolation) to 45.5% p-nitrophenol. The calculated and observed values agree well.

In Tables IX and X m-nitrophenol is considered as the solvent for one branch of the curve instead of the o- and p-nitrophenols, respectively. The Q for the m-nitrophenol may be calculated form a point on the curve of Figure 11.

TABLE X

The binary system: m-nitrophenol, p-nitrophenol

Mole fractions of m-Nitrophenol	Mole fractions of p-Nitrophenol	Freezing point °C Solvent Obs.	Freezing point °C Solvent Calc.	Eutectic observed	Solid phase
1.000	.000	93	—	—	First arrest m-nitrophenol, second eutectic
.909	.091	87.1	87.1	—	
.833	.167	82.6	81.8	—	
.769	.231	77.1	77.1	60.3	
.714	.286	74.1	—	60.1	
.667	.333	70.4	69.1	60.3	
.625	.375	67.1	65.5	60.6	
.571	.429	62.4	60.7	61.0	
					Eutectic
.527	.473	61.6	64.8	61.0	First arrest p-nitrophenol
.500	.500	66.3	68.1	60.8	
.455	.545	70.5	73.2	60.3	
.400	.600	77.8	79.5	60.5	
.334	.666	82.7	85.7	—	
.250	.750	91.6	93.5	—	
.143	.857	101.6	102.7	—	
.000	1.000	114	—	—	

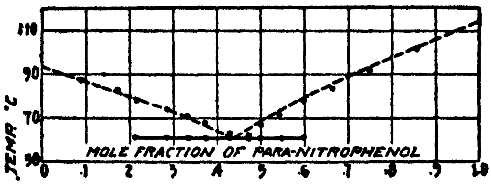

Fig. 11

Cooling Curve of the Binary Mixture: m-, p-Nitrophenol, calculated by Equation 6

Thus taking x = 0.714, T = 347.2 and putting T_o = 366 deg. A, we find

$$Q = 4210 \text{ cal. per mole.}$$

Assuming Q to remain constant and putting T_o = 366 deg. A in Equation 6, we have

$$T = \frac{921.1}{2.517 - \log_{10}x} \quad \ldots\ldots\ldots\ldots\ldots\ldots 12$$

This is the equation used in calculating the freezing points recorded in Tables IX and X where m-nitrophenol is considered the solvent.

The method of determining the ternary melting points was the same as that employed for the binary systems. The extrapolated binary eutectic was considered as one component and the isomer not included in the binary eutectic as the other component of a binary system. Successive amounts of the third isomer were added to lower the melting point of the eutectic mixture until no further lowering was noted on the addition of another portion of the third isomer.

The observed and calculated values for the three possible ternary systems are given in Tables XI, XII, and XIII. The various mole fractions of the ternary system in Table XI are made by adding to the binary eutectic ortho-, meta-nitrophenol, successive amounts of para-nitrophenol. Similarly, in Table XII, we have the binary eutectic ortho-, para-nitrophenol and meta-nitrophenol as the two components, also, in Table XIII, we have employed the binary eutectic para-, meta-nitrophenol for one component and the third isomer, ortho-nitrophenol, as the other component.

TABLE XI

The binary system: eutectic o-, m-nitrophenol, p-nitrophenol

Mole fractions of		Freezing point °C of eutectic		
Eutectic o-,m-nitrophenol	p-Nitrophenol	Observed	Calculated	Solid phase
1.000	.000	31.6	—	
.979	.021	28.8	30.7	Binary eutectic o-, m-nitrophenol
.959	.041	27.9	29.7	Binary eutectic o-, m-nitrophenol
.940	.060	27.1	28.8	Binary eutectic o-, m-nitrophenol
.922	.078	26.3	27.9	Binary eutectic o-, m-nitrophenol
.904	.096	25.7	26.9	Binary eutectic o-, m-nitrophenol
.887	.113	25.4	26.0	Binary eutectic o-, m-nitrophenol
.854	.146	24.4	24.3	Binary eutectic o-, m-nitrophenol
.824	.176	23.0	22.8	Binary eutectic o-, m-nitrophenol
.796	.204	21.8	21.2	Ternary eutectic

TABLE XII

The binary system: eutectic o-, p-nitrophenol, m-nitrophenol

Mole fractions of		Freezing point °C of eutectic		Solid phase
Eutectic o-,p-nitrophenol	m-Nitrophenol	Observed	Calculated	
1.000	.000	34.7	—	Binary eutectic o-, p-nitrophenol
.909	.091	29.5	30	Binary eutectic o-, p-nitrophenol
.833	.167	26.2	25.9	Binary eutectic o-, p-nitrophenol
.800	.200	23.5	24	Binary eutectic o-, p-nitrophenol
.770	.230	22.1	22.2	Binary eutectic o-, p-nitrophenol
.750	.250	21.3	21.1	Ternary eutectic

TABLE XIII

The binary system: eutectic p-, m-nitrophenol, o-nitrophenol

Mole fractions of		Freezing point °C of eutectic		Solid phase
Eutectic p-,m-nitrophenol	o-Nitrophenol	Observed	Calculated	
1.000	.000	61.	—	
.939	.061	57.2	57.1	Binary eutectic p-, m-nitrophenol
.896	.104	54.3	54.6	Binary eutectic p-, m-nitrophenol
.859	.141	51.9	52.4	Binary eutectic p-, m-nitrophenol
.824	.176	49.3	50.2	Binary eutectic p-, m-nitrophenol
.742	.258	44.8	45.3	Binary eutectic p-, m-nitrophenol
.709	.291	41.0	42.8	Binary eutectic p-, m-nitrophenol
.632	.378	37.5	37.4	Binary eutectic p-, m-nitrophenol
.586	.414	33.7	33.9	Binary eutectic p-, m-nitrophenol
.514	.486	28.1	28.0	Binary eutectic p-, m-nitrophenol
.472	.528	24.9	24.3	Binary eutectic p-, m-nitrophenol
.449	.551	21.4	22.1	Ternary eutectic

Calculation of the Ternary Eutectic Points

Since at the eutectic temperature the solid that crystallizes out is pure crystals of solute and solvent, that is, the mixture has a definite percent of pure solute and solvent, it seems logical to conclude that the heat of fusion of the eutectic is composed of two factors, (1) the mole fraction of the heat of fusion of one mole of the pure solute, and (2) the mole fraction of the heat of fusion of one mole of pure solvent. On this

theory, let x and y be the components of the eutectic, Q_x and Q_y be the mole heats of fusion of the pure components, P_x and P_y the mole fractions of the pure components of Q_e the heat of fusion of the eutectic mixture whose mole fractions are P_x and P_y. Then, the value of Q_e is given by the expression

$$Q_e = Q_xP_x + Q_yP_y \quad \ldots\ldots\ldots\ldots 13$$

Substituting the proper values in Equation 13, we have $Q_e = 3870$ cal. as the heat of fusion of one mole of the binary eutectic whose mole fractions are 0.7 and 0.3, respectively, of ortho- and meta-nitrophenol. On putting this value, 3870 cal., for Q and $T_0 = 304.6$ deg. A, the melting point of the eutectic, in Equation 6, we find

$$T = \frac{837.1}{2.779 - \log_{10}x} \quad \ldots\ldots\ldots\ldots 14$$

which is the equation used to calculate the freezing points of the eutectic o-, m-nitrophenol as one component and the p-nitrophenol as the other component of the ternary system ortho-, meta-, para-nitrophenol. These values are recorded in Table XI.

Similarly for the binary eutectic in which the eutectic mixture of meta-, para-nitrophenol is taken as one component and ortho-nitrophenol as the other component, we have from Equation 13 that $Q_e = 4090$ cal. as the heat of fusion of one mole of the eutectic whose mole fractions are 0.455 and 0.545 of para- and meta-nitrophenol, respectively. Substituting this value in Equation 6 for Q and putting $T_0 = 333.3$ deg. A, the melting point of the eutectic, we find

$$T = \frac{894.8}{2.684 - \log_{10}x} \quad \ldots\ldots\ldots\ldots 15$$

This equation was used to calculate the values recorded in Table XIII.

To calculate the lowering of the melting point of the binary eutectic temperature of o-, p-nitrophenol by the addition of successive amounts of m-nitrophenol, in which 0.73 and 0.27 are the mole fractions of the o- and p-nitrophenol, respectively, we have from Equation 13 that $Q_e = 3790$ cal.

as the eutectic heat of fusion per mole. Putting Q = 3790 and T_0 = 307.7 deg. A, the melting point of the pure binary eutectic, in Equation 6, we have

$$T = \frac{829.2}{2.695 - \log_{10}x} \quad \ldots\ldots\ldots\ldots\ldots \quad 16$$

The values calculated by this equation are given in Table XII.

The results of Tables XI, XII and XIII are shown graphically in Figures 12, 13 and 14, respectively.

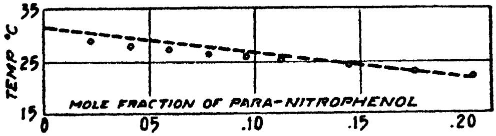

Fig. 12
Cooling Curve of the Binary System: Eutectic o-, m-Nitrophenol, p-Nitrophenol, calculated by Equation 6

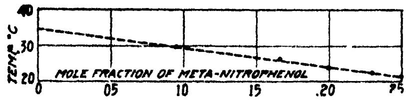

Fig. 13
Cooling Curve of the Binary System: Eutectic o-, p-Nitrophenol, m-Nitrophenol

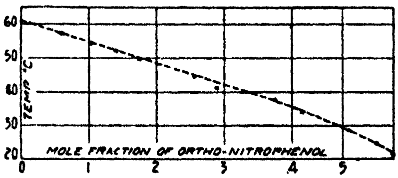

Fig. 14
Cooling Curve of the Binary System: Eutectic p-, m-Nitrophenol, o-Nitrophenol, calculated by Equation 6

The agreement between the observed and calculated values as seen by Figures 12, 13 and 14 are so close that the assumption we made, in computing the eutectic heat of fusion,

is justified. This assumption could only be entertained at the beginning on the ground that these place isomers in binary mixtures form ideal solutions when one dissolves in the other. If there had been any dissociating, associating or forming of compounds between the solute and solvent the calculation of the mole heat of fusion would not have been so simple. This method affords an easy means of calculating the ternary eutectic curve in the case of ideal solutions of organic isomers from a knowledge of the binary eutectic composition and temperature.

If we compare the equation of Hildebrand for calculating solubility with that derived by Washburn for the calculation of the freezing points of binary mixtures, we see that they are identical in form. The terms have the same significance, except in the solubility equation N denotes the mole fraction of the solute, while in the freezing point Equation 10, the analogous term, refers to the mole fraction of the component in excess and is called the mole fraction of the solvent. Both equations are based on the assumpton that the components of the solution in one case and the mixture in the other, are neither dissociated nor associated, and that the heat of fusion remains constant. Substances that are sufficiently alike chemically to form ideal solutions will follow these laws, that is to say solubility whenever the solution is ideal, is entirely independent of the nature of the solvent and is merely a function of the temperature. This equation may be used as a criterion to detect ideal solutions. In the case of the solubility of one mono-nitrophenol in the other it is evident that they are neither dissociated or associated as the observed and the calculated cooling curves agree excellently.

On comparing the right branch of the cooling curves in Figures 9 and 11 it is seen that the observed and calculated curve of the one holds for the other. The same is true of the left branch of the curves in Figures 9 and 10, and also, the left branch of the curves in Figure 11 and the right branch of the curves in Figure 10. These examples simply emphasize the fact that if there were no other factors governing solu-

bility, except temperature, when the cooling curve had once been determined, it would apply equally as well in the presence of all other substances.

Each of the cooling curves has a point of inflection. The greatest divergence between the observed and calculated curves is at this point. This may be due to some previous assumption as to the physical constants employed or chemical properties. The observed and calculated eutectic temperatures (extrapolated) agree within 0 deg. C to 4.5 deg. C and the compositions (extrapolated) only disagree by 0.03 of a mole fraction. This is quite gratifying but is what we should expect in the case of place isomers.

The eutectic horizontal in no case was traced to the pure components. Although the mixture became so stiff it could not be stirred, still liquid could be seen in the inter-crystalline spaces. Without doubt if the crystallized solvent could be filtered off the eutectic horizontal could be traced to the pure components. The freezing point of the eutectic mixture agrees well with the eutectic arrest in the freezing point of the various mixtures.

These cooling curves afford an excellent means of determining the purity of any one of the mono-nitrophenols when the impurity is either one of the other isomers. By simply determining the melting point and then referring to the proper cooling curve one can read off directly the mole fraction of the solvent corresponding to this temperature.

In Table XIV is shown the composition of the observed ternary eutectic mixtures as approached from the three binary eutectic mixtures.

TABLE XIV
Ternary eutectic composition

Composition of eutectic	Mole fraction of ortho-	Mole fraction of meta-	Mole fraction of para-	Observed eutectic temp., °C	Calculated eutectic temp., °C
o-, m-nitrophenol	.557	.239	.204	21.8	21.2
o-, p-nitrophenol	.546	.250	.204	21.3	21.1
m-, p-nitrophenol	.551	.249	.200	21.4	22.1
Average	.551	.246	.203	21.5	21.46

It seems that the composition is nearly the same no matter from which binary eutectic the ternary is approached. These values should be the same, but error was introduced in extrapolating the binary eutectic composition. The mean of the observed and calculated eutectic temperatures agrees almost perfectly. The variation of the components from their mean is in no case over 0.007 mole and in the case of the para-component is not over 0.003 mole.

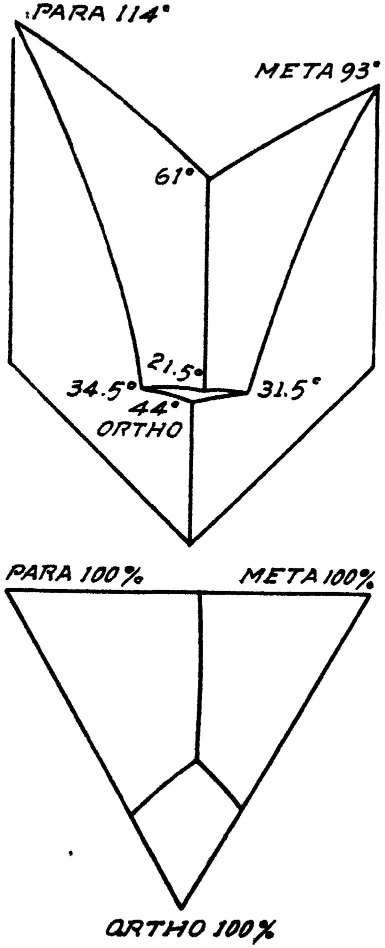

Fig. 15
o-, m-, p-Nitrophenol

From the three binary systems a space model illustrated in elevation and in projection on the base has been drawn. See Figure 15. The divisions representing the composition are in mole fractions.

There is but one ternary eutectic point. The solid phase ortho-, meta- and para-nitrophenol are in equilibrium with the liquid at a temperature of 21.5 deg. C.

Summary

1. It is shown that none of the methods proposed are suitable to predict the solubility of the three isomeric mono-nitrophenols in the common organic solvents acetone, benzene, ethyl alcohol, and ethyl ether.

2. The cooling curves for the different binary and ternary systems of the mono-nitrophenols have been determined experimentally and

found to compare favorably with the calculated form.

3. The law used to calculate the cooling curves for the binary mixtures is shown to be equally suited for calculating the cooling curves of the ternary mixtures.

4. The mono-nitrophenols in the presence of each other behave as ideal solutions.

5. Benzene is a good solvent to extract ortho-nitrophenol from aqueous solutions of the mono-nitrophenols.

Acknowledgment

In conclusion the writer wishes to express his thanks to Prof. O. W. Brown, under whose direction this work was carried out, for his suggestions and criticism, and also, Mr. C. O. Henke for his aid in preparing this paper for publication.

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ALIZARIN-IRON LAKES

BY ARTHUR W. BULL AND J. R. ADAMS

Biltz and Utescher[1] after a study of several color lakes came to the conclusion that a true ferric alizarate was formed when alizarin, dissolved in 0.8% sodium hydroxide, was shaken with hydrous ferric oxide. When Alizarin Red SW was shaken with hydrous chromic oxide a typical adsorption isotherm was secured and they concluded that in this case no compound was formed. The results of their work on ferric alizarate can also be interpreted as a case of adsorption and in view of the chemical similarity of iron and chromium it seemed reasonable to suppose that both lakes are adsorption complexes. The following experiments were conducted with the object of determining whether Biltz's ferric alizarate is really a true compound.

If sodium alizarate reacts with hydrous ferric oxide to form a ferric alizarate it must follow that sodium hydroxide will be liberated by the reaction. If we are dealing with an adsorption effect it is quite probable that the alizarin will be taken up as unchanged sodium alizarate and there will be no accumulation of NaOH in the solution. A determination of the amount of sodium hydroxide remaining in solution after the alizarin has been removed by ferric oxide may therefore enable us to settle the point at issue. If ferric alizarate were formed with the accompanying liberation of sodium hydroxide we might still find, however, that little NaOH was left behind in case the alkali were strongly adsorbed by the excess ferric oxide.

Our first experiment was, therefore, the determination of the adsorption isotherm at room temperature (22°) for NaOH by hydrous ferric oxide. The oxide was precipitated from ferric chloride by the addition of a slight excess of ammonium hydroxide and then purified by repeated washings

[1] Ber. deutsch. chem. Ges., 38, 4143 (1905).

and dialysis until no test for chlorides could be secured in the wash water with silver nitrate. Enough oxide was prepared at one time to complete the whole series of experiments and all results were obtained on the same lot, so the data are strictly comparable. To 25 cc of the hydrous ferric oxide suspension (equivalent to 0.8525 grams of Fe_2O_3) varying volumes of N/10 NaOH were added as given below and the mixtures were made up to constant volume (50.0 cc). The bottles containing the suspensions were shaken in an automatic device for ten hours, a control bottle indicating that this was ample time for the attainment of equilibrium. After shaking, the ferric oxide was allowed to settle and an aliquot portion of the supernatant liquid was titrated with hydrochloric acid.

TABLE I

Adsorption of NaOH by $Fe_2O_3 . x H_2O$

Cc N/10 NaOH start	Cc N/10 NaOH end	Cc N/10 NaOH adsorbed
1.20	0.20	1.00
2.40	0.56	1.84
3.60	1.07	2.53
4.80	1.52	3.28
6.00	2.13	3.87

At the higher concentrations it will be noted that about 40% of the NaOH is left unadsorbed.

Three grams of sublimed alizarin (M. P. 289°) were dissolved in a very slight excess of the theoretical quantity of NaOH and the solution was diluted to one liter. Diffusion experiments showed that we were dealing with a true solution. To fresh 25 cc portions of the ferric oxide suspension previously described, varying amounts of this sodium alizarate solution were added; the mixtures were diluted to the standard volume and shaking continued at room temperature until equilibrium had been reached. The relative quantities of dye and oxide were so chosen that practically complete adsorption of the dye occurred even at the highest concentrations. After shaking, the oxide was allowed to settle and the NaOH in an

aliquot portion of the supernatant liquid was determined by titration. The results are given below and in Fig. 1.

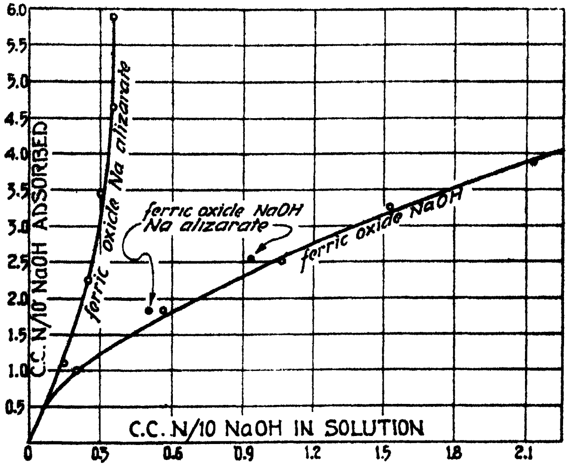

Fig. 1

TABLE II

Adsorption of Sodium Alizarate by Ferric Oxide

No.	Cc of sodium alizarate soln.	Cc N/10 NaOH equiv. to this sod. alizarate	Cc N/10 NaOH left in bath	Cc N/10 NaOH adsorbed
1	5.00	1.25	0.15	1.10
2	10.00	2.50	0.25	2.25
3	15.00	3.75	0.30	3.45
4	20.00	5.00	0.35	4.65
5	25.00	6.25	0.35	5.90

If ferric alizarate were formed, NaOH would be liberated as given in column 2. Much smaller quantities than these are found, however, and there is also much less sodium hydroxide present in the baths than would be found if the calculated amount of NaOH were formed and then independently adsorbed by the ferric oxide as in Table I. The small amount of NaOH found in the baths is probably due to hydrolysis of the adsorbed sodium alizarate, producing in solution the amounts of alkali shown, while the insoluble alizarin remains on the

adsorbent. The first few values are lower than the hydrolysis value because the hydrolysis will be determined to some extent by the intensity of adsorption. That is, if we start with a given quantity of ferric oxide and allow it to adsorb increasing quantities of sodium alizarate by placing it in successively increasing concentrations of the dye, the adsorbed material will be more strongly held when only a small amount is present than when a large amount has been taken up. The hydrolysis value will be lowered proportionately, analogous to the production of chemical inertness by adsorption.

Because of the small amounts of NaOH found, it seems probable that the dye has been taken up as sodium alizarate but two other possibilities should be considered. First the adsorption of NaOH may conceivably be increased by the adsorption of alizarin. To test this, two duplicates of No. 2 in Table II were prepared and N/10 NaOH was added as follows before shaking.

TABLE III
Adsorption of NaOH by Ferric Oxide in the Presence of Alizarin

Cc sodium alizarate solution	Cc N/10 NaOH added	Cc N/10 NaOH left	Cc N/10 free NaOH adsorbed	Cc N/10 NaOH adsorbed in absence of alizarin (Table I)
10	2.40	.50	1.90	1.84
10	3.60	.93	2.67	2.53

Comparison of the values in the last two columns shows that the effect of the alizarin on the adsorption of NaOH is slight. The differences are hardly beyond the experimental error. The second possibility is that a triple compound, sodium-ferric-alizarate may be formed. In view of the smooth curve obtained by Biltz this contingency seems remote. Our data also give no indication of such a compound. It therefore seems probable that the iron-alizarin lake, is, like the chromium lake, an adsorption complex.

Summary

Experimental evidence has been presented to show that the iron-alizarin lake of Biltz is not a true chemical compound,

ferric alizarate, but that it is an adsorption complex of hydrous ferric oxide and sodium alizarate.

This work was carried out under the direction of Professor Bancroft and we wish to express our thanks to him for many helpful suggestions and kindly criticism. This work was made possible by a grant from the Chemical Foundation.

Cornell University

ADSORPTION BY PRECIPITATES. V

BY HARRY B. WEISER

Adsorption during the Precipitation of Colloids by Mixtures of Electrolytes

The precipitation of colloids by mixtures of electrolytes was studied first by Linder and Picton[1] more than twenty-five years ago. Their results are interesting although they determined the precipitation values by a method which does not admit of the highest degree of accuracy. This method was as follows: Twenty-six cubic centimeters of a colloidal solution of arsenious sulphide was "titrated" by allowing electrolyte to flow drop by drop from a burette until precipitation was observed to be complete. The concentration of the several electrolytes was so chosen that approximately equal volumes were necessary to effect complete coagulation. This concentration was approximately fifty times greater for salts with univalent cations than for salts with divalent cations. To determine the precipitation value of a mixture of electrolytes, a certain fraction of the precipitation value of one electrolyte was added and the titration completed with a second. Thus, to coagulate 26 cc of colloidal As_2S_3 it was necessary to add either 4.9 cc of N/2 NH_4Cl or 4.2 cc of N/2 HCl; but on first adding 2 cc of the NH_4Cl solution only 2.4 cc of HCl were needed to complete coagulation, the calculated amount being 2.5 cc. Similar results were obtained with other mixtures of electrolytes as given in Table I.

From the results recorded in Table I, Linder and Picton concluded that when salts having cations of the same valence are added successively to produce coagulation the effect is additive. Experiments were next carried out with salts having cations of different valence. In Table II is recorded the results with potassium chloride and strontium chloride.

[1] Jour. Chem. Soc., 67, 67(1895).

TABLE I

Salt A	Volume A	Salt B	Volume B to complete coagulation		
			determined	calculated	difference
		HCl	4.20		
NH_4Cl	4.90				
NH_4Cl	2.00	HCl	2.40	2.50	—0.10
HCl	2.60	NH_4Cl	1.75	1.85	—0.10
		HNO_3	4.10		
HCl	2.35	HNO_3	1.97	1.80	0.17
		K_2SO_4	4.40		
HNO_3	2.00	K_2SO_4	1.95	2.25	0.30
NH_4Cl	2.00	K_2SO_4	2.40	2.60	0.20
$Ca(NO_3)_2$	4.60				
		$BaCl_2$	4.20		
$Ca(NO_3)_2$	2.20	$BaCl_2$	2.30	2.20	—0.10

TABLE II

Cc of KCl	Cc of $SrCl_2$ to complete coagulation		
	determined	calculated	difference
	4.40		
6.60			
0.30	4.90	4.20	0.70
0.60	5.40	4.00	1.40
0.90	5.50	3.80	1.70
1.20	5.55	3.60	1.95
1.50	5.70	3.40	2.30
1.80	5.90	3.20	2.70
2.10	6.00	3.00	3.00
2.40	5.70	2.80	2.90
2.70	5.65	2.60	3.05
3.00	5.30	2.40	2.90
3.30	5.10	2.20	2.90

The results given in Table II show that the effect is not additive when colloidal As_2S_3 is coagulated by the successive addition of salts of different valence. Referring to these observations Linder and Picton say: "Indeed, strange as it may seem the amount of strontium chloride needed for coagulation is actually increased by the previous addition of potassium chloride. We also observe that up to a certain point the more potassium chloride is added the more strontium chloride is needed to produce coagulation; but when the

proportion of potassium chloride exceeds this limit, any further addition of that salt begins to diminish the amount of strontium chloride needed to induce coagulation."

An observation of Freundlich[1] seems to be in line with the results of Linder and Picton recorded above. The former observed that the precipitation value of $BaCl_2$ for colloidal As_2S_3 was not changed appreciably in the presence of approximately one-tenth the amount of KCl necessary for complete precipitation. "To a liter of an As_2S_3 colloid containing 16.12 millimoles As_2S_3 per l. was added slowly a liter of a KCl solution containing 8.656 millimoles KCl per l. For this solution, which was quite clear, the precipitation value of $BaCl_2$ was 0.885 millimole per l. After taking into account the dilution by the KCl and $BaCl_2$ solutions the content of the colloid was 7.328 millimoles As_2S_3 per l. From the table which gives the dependence of the precipitation value on the content of the colloid, was obtained by interpolation a precipitation value of approximately 0.88 millimole $BaCl_2$ per l. Hence the addition of a small amount of KCl does not affect the precipitation value of $BaCl_2$."

Similar observations were made by Blake[2] on the amounts of mixtures of electrolytes necessary to convert red colloidal gold into blue.

No determinations have been made of adsorption during the precipitation of colloids by mixtures of electrolytes. However, some data are available on adsorption by solid from mixtures of solutes that are of interest in this connection. Thus, Masius[3] studied the simultaneous adsorption of mixtures of organic acids by blood charcoal and arrived at the conclusion that less of each was adsorbed than if the other was not present. In this connection Freundlich[4] remarks: "Particularly important today is the case of mixtures of two substances one

[1] Zeit. phys. Chem., **44**, 145 (1903).
[2] Am. Chem. Jour., **16**, 438 (1903).
[3] "Uber die Adsorption in Gemischen." Dissertation, Leipzig (1908).
[4] Kapillarchemie, 164 (1909).

of which is adsorbed much more strongly than the other, such as is found with benzoic acid and oxalic acid. But a small concentration of benzoic acid is sufficient to cut down the adsorption of oxalic acid to a very small value,—and yet the presence of the latter always manifests itself so that the benzoic acid is adsorbed appreciably less than from the pure solution. For example, although in a pure oxalic acid solution (in equilibrium with a $c = 0.17$ equivalent) $x/m = 2.5$ milliequivalents per gram of carbon, the presence of a concentration of 0.004 equivalents of benzoic acid is sufficient to decrease the x/m of oxalic acid (again in equilibrium with a $c = 0.17$) to 0.36 milliequivalent per gram; with this concentration of benzoic acid in equilibrium in the mixture, $x/m = 2.3$ milliequivalents per gram carbon while in pure solution the x/m would amount to 2.5. This is a typical case of a "poisoning" action; if carbon should catalyze a reaction of oxalic acid, a small amount of benzoic acid would be sufficient to cut down the amount of oxalic acid adsorbed and therewith the amount reacting, to a fraction of the original."

Schmidt[1] studied the simultaneous adsorption of iodine and acetic acid from solutions in both water and ethyl acetate; and like Masius, he found that less of each was adsorbed than if the other had not been present. Similarly, Lachs and Michaelis[2] observed that the presence of KOH cuts down the adsorption of KCl by charcoal from water solution; Freundlich and Kempfer[3] found that thorium salts decreased the adsorption of uranium X by charcoal; and Rona and Michaelis[4] observed that acetone and acetic acid decreased the adsorption of grape sugar by charcoal. From these observations, it would seem that each of two solutes is always adsorbed less than if the other were absent. This statement is not true as it stands, as Lachs and Michaelis[5] observed that the presence

[1] Zeit. phys. Chem., **74**, 730 (1910).
[2] Zeit. Elektrochemie, **17**, 1 (1911).
[3] Zeit. phys. Chem., **90**, 681 (1915).
[4] Biochem. Zeit., **16**, 499 (1909).
[5] Loc. cit.

of a small amount of sulphuric acid increased the amount of chloride adsorbed from KCl solution. In this case the presence of the strongly adsorbed hydrogen ion increased the adsorption of chloride ion. The rule seems to be general that an anion is adsorbed more strongly in the presence of a readily adsorbed cation and a cation is adsorbed more strongly in the presence of a readily adsorbed anion.[1]

The results of investigations on the simultaneous adsorption by solids of mixtures of electrolytes may be summarized as follows: From a mixture of two electrolytes having no ion in common, the most strongly adsorbed cation and anion is taken up most and the other pair least readily; from a mixture of electrolytes having one ion in common, the oppositely charged ions are each adsorbed less than if the other were absent but the most readily adsorbed ion is displaced the least. We will now consider the phenomenon of adsorption during the precipitation of colloids with mixed electrolytes.

Theoretical

The addition of a suitable concentration of electrolyte to a colloid stabilized by preferential adsorption of a given ion, usually results in precipitation owing to neutralization of the charged particles by adsorption of ions of opposite charge. The ion of an electrolyte which causes neutralization by adsorption is usually referred to as the precipitating ion. If the ion having the same charge as the colloid is adsorbed it tends to stabilize the colloid and is called the stabilizing ion. The stabilizing influence of the ion having the same charge as the colloid is frequently so slight relatively, that it may be neglected altogether; but this is by no means true in every case. The adsorption of equivalent amounts of all precipitating ions will effect neutralization of a given amount of colloid only in case the stabilizing action of the ion having the same charge as the colloid is negligible. The concentration of different electrolytes necessary to cause precipitation of a given colloid

[1] Estrup: Zeit. Kolloidchemie, 11, 8 (1912); Bancroft: Jour. Phys. Chem., 18, 1, 118, 385 (1914).

is influenced by a number of factors[1] most important of which are the differences in the adsorbability of the precipitating ions and of the stabilizing ions. On account of these differences in adsorbability, different electrolytes precipitate a given colloid in widely varying concentrations. Neglecting the effect of the stabilizing ion, neutralization by a mixture of any two electrolytes is accomplished by the simultaneous adsorption of equivalent amounts of the two precipitating ions in a varying ratio. The ratio varies since the amounts of the two ions adsorbed depend on the concentration and adsorbability of each, together with the effect the presence of each has on the adsorption of the other. The influence of the stabilizing ion can not be neglected in case it is adsorbed in amount that is appreciable compared to the adsorption of the original ion which gives the colloid its stability. These several effects will be brought out in the experiments to be described in the next section.

Experimental

Since the method of procedure followed by Linder and Picton in the determination of precipitation values is unsatisfactory, a series of experiments was carried out on the precipitation of colloidal arsenious oxide and colloidal hydrous ferric oxide by the simultaneous addition of two electrolytes.

Precipitation of Colloids with Mixtures of Electrolytes

Method of Procedure.—Colloidal arsenious sulphide was prepared by passing hydrogen sulphide through a solution of arsenious oxide, after which the excess hydrogen sulphide was removed with a current of hydrogen. Colloidal hydrous ferric oxide was prepared by the hydrolysis of ferric acetate as described in detail in an earlier paper.[2] The precipitation values were determined as follows: A definite volume of a solution of known strength was measured into a test-tube using a 2 cc Ostwald pipette graduated in tenths of a cc. This was diluted with water to 10 cc and was poured rapidly into

[1] Weiser and Middleton: Jour. Phys. Chem., 24, 68 (1920).
[2] Weiser: Ibid., 24, 277 (1920).

another test-tube containing 10 cc of colloid. After shaking thoroughly, the mixture was set aside and examined subsequently to determine whether precipitation was complete. In the case of the colloidal sulphide the mixture was allowed to stand two hours after which it was shaken and filtered into a small Nessler tube. The process was repeated until the filtrate just failed to show the greenish opalescence characteristic of the dilute colloid. With the colloidal ferric oxide the mixture was allowed to stand 12 hours after which the supernatant liquid was poured through a filter into a Nessler tube and examined. The precipitation value of mixtures of electrolytes was determined in a similar manner. It was customary to use a definite volume of one electrolyte and to vary the volume of the other until the required amount was found. In every case, however, the mixture of electrolytes was diluted to 10 cc before adding to 10 cc of colloid.

Experiments with Colloidal As_2S_3 (a).—The first experiments were carried out with colloidal As_2S_3 using mixtures of N/2 potassium chloride and N/50 strontium chloride. The values given in Table III represent the number of cubic centimeters of the respective solutions that were mixed, diluted to 10 cc and added to 10 cc of colloid, causing complete coagulation in 2 hours.

TABLE III

Precipitation of Colloidal As_2S_3 with Mixtures of KCl and $SrCl_2$

N/2 KCl taken	N/50 $SrCl_2$ to complete coagulation		
	determined	calculated	difference
2.82			
	1.50		
0.50	1.92	1.23	0.69
1.00	1.80	0.97	0.83
1.50	1.35	0.70	0.65
2.00	0.68	0.44	0.24
2.50	0.28	0.18	0.10

Experiments similar to the above were carried out with mixtures of N/50 $SrCl_2$ and N/50 $BaCl_2$. The results are given in Table IV.

TABLE IV

Precipitation of Colloidal As_2S_3 with Mixtures of $SrCl_2$ and $BaCl_2$

N/50 $SrCl_2$ taken	N/50 $BaCl_2$ to complete coagulation		
	determined	calculated	difference
1.50			
	1.78		
0.50	1.20	1.19	0.01
1.00	0.62	0.59	0.03

The above results confirm Linder and Picton's observations that the precipitating action of a mixture of electrolytes is additive in case the precipitating power of the ions is of the same order of magnitude such as usually obtains with ions of the same valence; but is far from additive in case the precipitating power of the ions varies widely as is usual with ions of different valence.

Experiments with Colloidal Hydrous Ferric Oxide(*a*).—The first precipitation experiments with colloidal hydrous ferric oxide were carried out with mixtures of N/2 KCl and N/65 $K_2C_2O_4$. Since the colloidal oxide is positively charged, the anions are the precipitating ions. In this case the usual difficulty was experienced in determining the precipitation value with KCl. For reasons to be given later, 5 cc of KCl in a total volume of 20 cc is taken as the precipitation concentration for the purpose of making the calculations given in column 3 of Table V, although precipitation was incomplete in 12 hours in the presence of a much larger concentration of

TABLE V

Precipitation of Colloidal Fe_2O_3 with Mixtures of KCl and $K_2C_2O_4$

N/2 KCl taken	N/65 $K_2C_2O_4$ to complete coagulation		
	determined	calculated	difference
5.0			
	1.15		
1.0	0.78	0.92	0.14
2.0	0.60	0.69	—0.09
3.0	0.53	0.56	—0.03
4.0	0.29	0.23	0.06

KCl. No difficulty whatsoever was encountered in getting the precipitation value for potassium oxalate or for mixtures of potassium oxalate and chloride.

Similar experiments were carried out with mixtures of potassium sulphate and potassium oxalate with the results given in Table VI.

TABLE VI

Precipitation of Colloidal Fe_2O_3 with Mixtures of $K_2C_2O_4$ and K_2SO_4

N/65 $K_2C_2O_4$ taken	N/50 K_2SO_4 to complete coagulation		
	determined	calculated	difference
1.15			
	0.65		
0.50	0.30	0.28	0.02

The results recorded in Tables V and VI indicate that with colloidal hydrous ferric oxide the precipitating action of a mixture of ions is almost additive not only with ions that precipitate in approximately the same concentration but with those of widely varying precipitating power. This result was altogether unexpected in view of the experiments on the precipitation of colloidal As_2S_3 by the simultaneous addition of the chlorides of strontium and potassium. A possible explanation of the difference was suggested by the behavior of colloidal ferric oxide in the presence of KCl. It was observed repeatedly that a large excess of this salt was necessary to precipitate the last trace of the colloid within 24 hours. This was shown quantitatively in the following experiment.

Precipitation of Colloidal Hydrous Ferric Oxide with KCl.— To 100 cc portions of colloidal hydrous ferric oxide containing 1.65 g of Fe_2O_3 per liter were added 100 cc of KCl of varying concentrations. The mixtures were placed in wide-mouthed bottles of 250 cc capacity. With the lower concentrations of KCl the precipitations were far from complete in 24 hours so that all mixtures were allowed to stand 48 hours, after which each was centrifuged for 15 minutes at 3000 r. p. m. By this process the precipitated ferric oxide was matted firmly in the

bottom of the bottle so that the supernatant solution could be poured off. This was done and the remaining ferric oxide was precipitated with ammonia and determined gravimetrically in the usual way. The results are given in Table VII.

TABLE VII

Cc of solutions mixed			Fe_2O_3 in colloidal state after 48 hours
colloid	water	N/2 KCl	
100	55	45	0.0158
100	50	50	0.0138
100	45	55	0.0116
100	40	60	0.0106
100	35	65	0.0098
100	30	70	0.0075
100	25	75	0.0067

From the above results it will be seen that with 45 cc of KCl in 200 cc approximately one-tenth of the colloid remained unprecipitated in 48 hours. The amount was less and less as the concentration of KCl was increased but was still appreciable with 75 cc of KCl. It is evident, therefore, that at a certain concentration of KCl most of the colloid under consideration is precipitated but above this point a very large excess is necessary to effect complete precipitation. Since such a large excess of KCl is necessary to coagulate the trace of colloid that would require but a very small amount of potassium oxalate, it is difficult to decide what value should be taken as the precipitation concentration for KCl in making the calculations recorded in column 3 of Table V. I have taken 5 cc of KCl in 20 cc since this precipitated a large portion of the colloid in 12 hours.

Experiments with Colloidal Hydrous Ferric Oxide (*b*).—The doubtful accuracy of the results on the precipitation of colloidal ferric oxide with a mixture of electrolytes, one of which was KCl, lead to a repetition of the precipitation experiments substituting potassium sulphate for the oxalate and potassium bromate for the chloride. The bromate precipitates in much lower concentration than the chloride and gives a comparatively

sharp precipitation value. The results of a series of experiments are given in Table VIII. As before, the values in the table represent the number of cubic centimeters of electrolytes which cause complete coagulation in 12 hours when mixed, diluted to 10 cc and added to 10 cc of colloid.

TABLE VIII

Precipitation of Colloidal Fe_2O_3 with Mixtures of $KBrO_3$ and K_2SO_4

N/4 $KBrO_3$ taken	N/50 K_2SO_4 to complete coagulation		
	determined	calculated	difference
3.25			
	0.65		
1.00	0.41	0.45	—0.04
2.00	0.25	0.25	0.00
2.50	0.15	0.20	—0.05

Again it will be noted from the above results that the precipitating action of a mixture of the two electrolytes is nearly additive, the determined values being a trifle less than the calculated instead of very much greater as in the case of colloidal As_2S_3.

Experiments with Colloidal $As_2S_3(b)$.—In order to be certain that the results with colloidal As_2S_3, given in Table III, were correct the experiments with this colloid were repeated using $BaCl_2$ instead of $SrCl_2$. A period of three months elapsed between the two series of experiments and the colloid was somewhat less stable as is evidenced by the somewhat lower precipitation values recorded in Table IX.

TABLE IX

Precipitation of Colloidal As_2S_3 with Mixtures of KCl and $BaCl_2$

N/2 KCl taken	N/50 $BaCl_2$ to complete coagulation		
	determined	calculated	difference
2.65			
	1.70		
0.50	2.40	1.38	1.02
1.00	2.32	1.06	1.26
1.50	1.95	0.74	1.21
2.00	1.23	0.42	0.81

The results recorded in Table IX confirm the results given in Table III, that the precipitating action of mixtures of ions for colloidal As_2S_3 is not additive in case the precipitating power of the ions shows wide variation. Since the behavior is quite different with colloidal hydrous ferric oxide under similar conditions, some experiments were carried out on the adsorption of precipitating ions during the precipitation of colloids by mixtures of electrolytes.

Experiments on Adsorption

Adsorption by Hydrous Ferric Oxide.—The method of determining adsorption during the precipitation of colloidal hydrous ferric oxide has been described in detail in former papers.[1] This method consists essentially in precipitating a definite amount of colloid with a known concentration of electrolyte and determining the amount of electrolyte unadsorbed. In the following experiments, 100 cc portions of colloid containing 1.65 grams Fe_2O_3 per liter were precipitated with 50 cc of mixtures containing a constant amount of $K_2C_2O_4$ and varying amounts of either KCl or K_2SO_4. After precipitation the mixtures were placed in 250 cc wide-mouthed bottles and allowed to stand for 1 hour, after which they were centrifuged for 15 minutes at 3000 r. p. m. The supernatant liquids were poured off quantitatively and the inside of the vessels rinsed taking care not to dislodge the hydrous oxide matted in the bottom of the bottles. For the purpose of these experiments it was unnecessary to wash the precipitates. The supernantant liquids were each diluted to 200 cc and the oxalate determined with standard permanganate following the same procedure used in the standardization. The results are given in Tables X and XI. In these tables the adsorption of oxalate under various conditions is expressed in cubic centimeters of N/50 solution carried down during the precipitation of 100 cc of colloid containing 0.165 grams of Fe_2O_3.

[1] Weiser and Middleton: Jour. Phys. Chem., 24, 30 (1920); Weiser: Ibid., 25, 399 (1921).

TABLE X

Adsorption of Oxalate in the Presence of Chloride

Mixture added to 100 cc colloid			Cc N/50 oxalate remaining	Cc N/50 oxalate absorbed
Cc N/50 $K_2C_2O_4$	Cc N/2 KCl	Cc H_2O		
13.0	0.0	37.0	2.35	10.65
13.0	15.0	22.0	2.35	10.65
13.0	20.0	17.0	2.41	10.59
13.0	35.0	2.0	2.55	10.45

TABLE XI

Adsorption of Oxalate in the Presence of Sulphate

Mixture added to 100 cc colloid			Cc N/50 oxalate remaining	Cc N/50 oxalate adsorbed
Cc N/50 $K_2C_2O_4$	Cc N/10 K_2SO_4	Cc H_2O		
12.25	0.00	37.75	1.81	10.44
12.25	0.20	37.55	1.86	10.39
12.25	3.00	34.75	4.16	8.09
12.25	9.00	29.75	5.39	6.86

The above results show that the adsorption of oxalate is decreased but slightly by the presence of a comparatively large amount of KCl whereas K_2SO_4 in comparatively small amounts decreases appreciably the oxalate adsorption. However, the adsorption of oxalate is reduced but slightly by a very small amount of sulphate.

Adsorption by Arsenious Sulphide.—Adsorption during the precipitation of colloidal As_2S_3 was determined in much the same way as the similar experiments with colloidal ferric oxide: 100 cc portions of colloid containing 1.76 grams As_2S_3 were precipitated with $BaCl_2$ and with mixtures of $BaCl_2$ and KCl. After standing for 1 hour the mixtures were centrifuged and the supernatant solutions removed from the precipitate quantitatively and analyzed for barium by the usual gravimetric method. All analyses were carried out under conditions as nearly constant as possible. The precipitation was made always in the same volume and in the presence of the same amount of HCl and KCl. It was necessary to add the required amount of KCl to the supernatant liquid which was free from

it originally. In this way all determinations of barium were comparable. The results are given in Table XII.

Table XII

Adsorption of Barium in the Presence of Potassium

Mixture added to 100 cc colloid			Gm $BaSO_4$ remaining		Cc N/50 $BaCl_2$ remaining	Cc N/50 $BaCl_2$ adsorbed
Cc N/50 $BaCl_2$	Cc N KCl	Cc H_2O				
25.0	0.0	25.0	0.0389	0.0389	16.65	8.35
25.0	0.0	25.0	0.0390			
25.0	25.0	0.0	0.0470	0.0471	20.16	4.84
25.0	25.0	0.0	0.0472			

From the above results it is evident that the adsorption of barium ion is decreased materially by the presence of excess potassium ion. It should be pointed out that the adsorption experiments using colloidal As_2S_3 are not strictly comparable with the experiments using colloidal hydrous ferric oxide since the adsorption of the former is not so great as that of the latter and it was necessary to use a more concentrated As_2S_3 colloid. However, the ratio of the concentration of $K^{\cdot}$ to $Ba^{\cdot\cdot}$ is less in the experiments recorded in Table XII than the ratio of the concentration of Cl' to C_2O_4'' in experiment 4, Table X; yet the adsorption of $Ba^{\cdot\cdot}$ is appreciably decreased by the presence of $K^{\cdot}$ while that of C_2O_4'' is changed but slightly by the presence of Cl'.

Discussion of Results

It has been demonstrated that the precipitating action of mixtures of electrolytes for both colloidal hydrous ferric oxide and arsenious sulphide shows an additive relationship if the precipitating power of each is similar. Thus potassium sulphate and potassium oxalate precipitate colloidal ferric oxide at concentrations that are of the same order of magnitude and the precipitating action of mixtures of these two electrolytes is approximately additive. With mixtures of electrolytes that precipitate colloidal ferric oxide in almost the same concen-

tration, and have cations in common, the action of the anions only, need be considered. Since the precipitating power of each anion is of the same order of magnitude, they are adsorbed to a similar degree. If the precipitating power of mixtures of the two is additive we should expect the adsorption of each one to be affected but slightly by the presence of the other within the limits of the precipitation concentration. On the other hand, we should expect the adsorption of one ion to be decreased by the presence of an excess of the other above the precipitation concentration in proportion to the excess present. The accuracy of these deductions is indicated by the experiments, recorded in Table XI, on the adsorption of oxalate in the presence of varying amounts of sulphate.

Two cases have arisen in the above experiments on the precipitation of colloids by mixtures of electrolytes which precipitate in widely varying concentrations: With colloidal hydrous ferric oxide the precipitating action of mixtures of KCl or $KBrO_3$ with $K_2C_2O_4$ or K_2SO_4 approaches an additive relationship as shown in Tables V and VIII; while with colloidal arsenious sulphide the precipitating action of mixtures of KCl with $BaCl_2$ or $SrCl_2$ is not additive as shown in Tables III and IX. In the latter case there is an "antagonistic" influence in the sense that a certain concentration of KCl may require an amount of $BaCl_2$ or $SrCl_2$ appreciably greater than if no KCl had been added. Two factors must be considered in accounting for these phenomena: the effect of each precipitating ion on the adsorption of the other and the stabilizing action of the ion having the same charge as the colloid.

Disregarding the stabilizing action of the ion having the same charge as the colloid, we may consider the effect of each precipitating ion on the adsorption of the other. In the above experiments with colloidal hydrous ferric oxide, the precipitation concentration of KCl or $KBrO_3$ is shown to be very much greater than that of $K_2C_2O_4$ or K_2SO_4. We might expect the addition of a relatively large amount of chloride or bromate to decrease appreciably the adsorption of oxalate or sulphate which are present in such low concentration within the region

of the precipitation value. As a matter of fact, however, the adsorption of oxalate is decreased but slightly in the presence of a relatively high concentration of chloride as shown by the results recorded in Table X; hence, just as might be expected, the precipitating action of mixtures of salts of these ions is not far from additive. Different conditions obtain with colloidal arsenious sulphide. In this case the adsorption of the divalent barium ion is appreciably diminished in the presence of an excess of potassium ion as shown in Table XI; and at the same time, the adsorption of potassium ion is unquestionably diminished by the presence of barium. Accordingly the precipitating action of mixtures of salts of these ions is not additive but a relatively higher concentration of barium ion is necessary to secure neutralization by adsorption in the presence of potassium ion.

Another factor which must be considered is the influence of the stabilizing ion. The precipitation value of an electrolyte for a given colloid is that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the electrolyte in question. Thus colloidal arsenious sulphide probably owes its stability to preferential adsorption of the univalent HS' ion derived from the primary dissociation of H_2S. If enough potassium chloride is added to this colloid, the adsorption of $K^{\cdot}$ ion will neutralize the combined adsorption of the stabilizing ions, HS' and Cl'. In this particular case the high precipitation value of KCl may be due to the adsorption of Cl' being comparable at certain concentrations to the adsorption of $K^{\cdot}$. Indeed it is possible, but not proven, that at certain concentrations of KCl considerably below the precipitation value, the adsorption isotherm for Cl' may coincide with or even fall below that of $K^{\cdot}$. Within this region the addition of a small amount of the strongly adsorbed $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ may so decrease the adsorption of $K^{\cdot}$ that the adsorption isotherm for the latter will fall appreciably below that for Cl' as shown diagrammatically in Figure I. If this were true, in the region between *a* and *b*

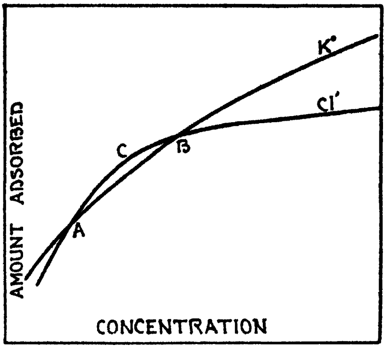

Fig. 1

in the diagram, the colloid will be relatively more stable than if no electrolytes were added. Hence within a certain region, the addition of KCl to colloidal As_2S_3 will increase rather than decrease the amount of $BaCl_2$ or $SrCl_2$ necessary to effect complete coagulation. Unfortunately we have no direct proof of this hypothesis; but there are certain facts in line with it. In the first place the presence of certain concentrations of KCl seems to produce a wider variation between the observed and calculated values for $SrCl_2$ and $BaCl_2$ than can be accounted for simply by the effect of $K^{\cdot}$ on the adsorption of $Ba^{\cdot\cdot}$ or $Sr^{\cdot\cdot}$ and vice versa. Secondly, with increasing concentration of KCl the stability of the colloid seems to approach a maximum (point *c* in the diagram) as is evidenced by a maximum variation between the observed and calculated values for $SrCl_2$ and $BaCl_2$.

In the experiments on the precipitation of colloidal As_2S_3 with mixtures of electrolytes of widely varying precipitating power, it is probable that both of the above-mentioned influences contribute to produce the wide variation between the observed and calculated values; while with colloidal hydrous ferric oxide neither is operative to any large extent and so the precipitating action of certain mixtures of electrolytes with widely varying precipitating power shows more nearly an additive relationship.

It may be asked why, in the case of colloidal As_2S_3 the adsorption of $Ba^{\cdot\cdot}$ is appreciably diminished by the presence of a relatively large amount of $K^{\cdot}$, while in the case of colloidal Fe_2O_3, the adsorption of C_2O_4'' is not influenced greatly by an excess of Cl'. The following explanation is suggested: It has been pointed out that a high precipitation value of an electrolyte can arise either from weak adsorption of the precipitating ion or from fairly strong adsorption of the precipitating ion associated with relatively strong adsorption of the stabilizing ion. In the case of colloidal Fe_2O_3 the adsorption of Cl' may be quite small while in the case of colloidal As_2S_3 the adsorption of both $K^{\cdot}$ and Cl' may be relatively quite large. This would account for a high precipitation value of KCl for both colloids and also would account for the fact that the adsorption of the strongly adsorbed $Ba^{\cdot\cdot}$ is diminished appreciably by the presence of $K^{\cdot}$ while the adsorption of the strongly adsorbed C_2O_4'' is influenced but slightly by an excess of Cl'.

Summary

The following is a brief summary of the results of this investigation:

(1) A study has been made (*1*) of the precipitation of colloidal hydrous ferric oxide and colloidal arsenious sulphide by the simultaneous addition of certain pairs of electrolytes and (*2*) of the adsorption of certain ions during the precipitation of the colloids with mixtures of electrolytes.

(2) The precipitating action of mixtures of pairs of electrolytes is approximately additive if the precipitating power of each is of the same order of magnitude; but may be far from additive if the electrolytes have widely varying precipitating power. In the latter case the action of the electrolytes is "antagonistic," in the sense that relatively more of each is necessary than if the other were absent.

(3) In the simultaneous adsorption by solids from mixtures of two electrolytes having no ion in common, the most strongly adsorbed cation and anion are taken up most and the other

pair least readily; from mixtures having one ion in common, the oppositely charged ions are each adsorbed less than if the other were absent but the most readily adsorbed ion is displaced the least.

(4) Factors which influence the precipitating action of mixtures of electrolytes are (*1*) the effect of the presence of each precipitating ion on the adsorption of the other and (*2*) the stabilizing action of the ions having the same charge as the colloid. The second factor is of minor importance with mixtures of electrolytes that have similar precipitation values and have stabilizing ions in common.

(5) The precipitating action of mixtures of electrolytes having similar precipitating power is additive since the adsorption of the precipitating ions is similar and so the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration.

(6) With mixtures of electrolytes of widely varying precipitating power, the precipitating action may be approximately additive in case the influence of both factors referred to in (4) is small; but may be far from additive in case the influence of both factors is large. These extreme cases have been realized experimentally.

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NEW BOOKS

The Chemical Effects of Alpha Particles and Electrons. *By S. C. Lind. 23 × 15 cm; pp. 182. New York: The Chemical Catalog Company, 1921. Price: $3.00.*—The American Chemical Society has adopted the admirable policy of publishing two sets of monographs, a scientific series and a technological series. These monographs are intended both to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line; and to promote research in that branch by furnishing a well-digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. This book by Mr. Lind is the first one of either series to be reviewed in the Journal of Physical Chemistry.

The chapters are entitled: radiochemistry; brief outline of radioactivity and some properties of the radiations; electrical effects and ionization; qualitative radiochemical effects; chemically quantitative investigations in liquid systems; reactions produced by radium emanations (first experiments); relation between gaseous ionization and radiochemical effects; kinetics of the chemical reactions produced by radium; additional relationships of the radiochemical effects; photochemical equivalence law; positive rays and recoil atoms; atomic disintegration by alpha particles.

On p. 17 the author states that "the term radiochemistry has already been used otherwise by some authors to designate the chemistry of the radioactive elements and of their transformations by atomic disintegration. Since this more special usage is relatively new and not thoroughly intrenched, and since the term radiochemistry is the only logical one to conform with such terms as electro-, thermo-, photo-chemistry and radiotherapy, it appears desirable to adopt the use of the term radiochemistry in the broader sense, exactly analogous to and including that of photochemistry, in the sense that all relations between chemical energy and any form of radiant energy or matter should be comprehended by the term radiochemistry.

"In the strictest sense, perhaps radiochemistry should deal only with truly radiated energy to the exclusion of the kinetic energy of projected particles of matter such as α particles or of electrons and β particles. This would practically narrow the subject to that of photochemistry itself. It is not only a matter of convenience to include also the relations involving material particles, but the relationships and reactions are in many ways so similar, and the analogies of such far-reaching importance, that it forms one of the chief objects of the present work to treat both from the same standpoint, without any particular distinction as to the vehicle of the radiated energy."

On p. 38 we read that "in connection with the measurement of gaseous ionization by means of saturation current, it should be pointed out that while the practice among physicists of referring to the total number of pairs of ions is fairly common, the expression ions where pairs of ions is meant is also unfortunately prevalent. This is particularly confusing to the chemist who in dealing with electrolytic ions in connection with the solution theories always means

total positive and negative ions, never ions of only one sign. Naturally the physicist in taking current units as the measure of gaseous ionization is prone to neglect the other half of the ionization, thus leading to confusion in cases where the number of ions of both signs is important."

The author is not very encouraging as to the coloring of glass and minerals by radium rays, p. 50. "It does not appear possible at present to formulate a satisfactory theory of the coloring effects, nor to decide whether they are chemical or physical in nature. Very great difficulties are encountered in trying to ascribe the color to any definite component, though it seems to be rather generally agreed that the presence of impurities, possibly in extremely minute quantity beyond the range of chemical determination, influences the color production. This would be suggested by the erratic differences found for the same mineral from different localities. Goldstein estimates that impurities amounting to not more than one part in a million produce color effects under the influence of cathode rays. The confusion that arises in attempting to settle on some certain component or impurity as responsible for the color may be illustrated by some of the following observations. Meyer and Przibram report that they have observed the production of the violet and of the brown color simultaneously on different parts of the same glass vessel, which were subjected to a difference only in the intensity of the radiation; while, in general, difference in intensity or even the kind of radiation influences only the rate at which color is produced. An outer glass tube enclosing an inner one (of the same glass) containing radium salt, takes on the same color as the inner one, though more slowly, although the outer one receives no α radiation and a different intensity of penetrating radiation from that received by the inner one. Hard glasses high in silica, of the pyrex or Jena type, invariably take the brown color, but silica vessels, including the transparent variety made from pure fused quartz, take the same violet color as ordinary soft glass. Lead glass is colored brown. In all cases the glass appears finally to become saturated and the color no longer deepens. Thick layers of glass appear to be more intensely colored on account of the depth of layer. Very thick glass, like the walls of a desiccator, becomes almose opaque upon prolonged radiation. The power of luminescing diminishes as the coloring increases.

"The color produced in glass and minerals by radium rays and by cathode rays can be discharged by heating almost to the softening point of glass. The same color is again restored by renewed radiation, and the cycle may be repeated apparently indefinitely, without any fatigue effect. . . . .

"It has been found by many observers that salts, glass, minerals, and other substances after being exposed to radium or to cathode rays become luminous in the dark at temperatures from 40° to 200° C. This appears to be due to an effect of the radiation which is as yet little understood. The mistake has been rather commonly made of supposing that there is a close connection between the discharge of color produced in glass, for instance (see preceding paragraph), and the thermoluminescent effect. However, it has recently been pointed out by Lind that thermoluminescence can usually be exhausted at about 200° without at all diminishing the color, which is not discharged from ordinary violet-colored glass below 400° to 500° C, so that there is evidently no direct connection between the two effects. Meyer and Przibram have made an interesting observation which has been confirmed by Lind that, if glass colored brown by radium

radiation be heated gently until its thermoluminescence is exhausted, its color is changed to the more common violet tint which then behaves as in glass originally colored violet, except that no further thermoluminescence is exhibited. Upon renewed radiation the color returns to brown.

"Freshly radiated glass will show thermoluminescence to the well-rested eye at a temperature quite below the boiling point of water, while glass which has been kept for three or four years after exposure must be raised to the neighborhood of 200° before luminescence sets in.

"From the foregoing statements it appears that if the coloration and thermoluminescence of glass and minerals are due to chemical causes, at least two different sets of reactions are involved which may have little or no connection with each other. The whole subject presents an attractive field for further investigation."

The chemical action of the alpha rays is apparently not a matter of absorption, p. 58. "The wide variety of chemical actions brought about, particularly by the α rays, is surprising and one must be struck by the universality of the phenomenon of chemical change by corpuscular radiation. This is in marked contrast with photochemical action, where the specific nature of the reaction and of the system being acted on depends entirely upon the wave length of the light, and its capability of being absorbed by the given system. The highly specific and selective nature of photochemical reactions is their chief characteristic; whereas, we find that α and β rays, in their passage through molecules, are almost universally capable of changing them chemically; their action does not depend upon any reciprocal relation with the atom or molecule affected, similar to a resonance effect. Owing to the tremendous kinetic energy of the α particles they always ionize and frequently produce chemical changes in the substances through which they pass. Several different views have been expressed regarding the mechanism of the reactions, which may be classified in general terms as: catalytic, mechanical and electrical."

As against this it is interesting to note one effect of the penetrating beta and gamma rays, p. 64. "The effect of penetrating radiation on toluene, both in the presence and absence of water, has been determined by Kailan, using 80 mgs of Ra element for a period of two years. The products of reaction in the presence of air were benzaldehyde, benzoic acid, and probably formic acid. In the case of dry toluene, less than $^1/_4\%$ was changed in two years. Effects of the same kind and magnitude could be obtained by 22 hours' radiation with a quartz mercury lamp at 8 cms. The effect of the penetrating rays from 110 mgs of element in two years on 50 cc each of toluene and water produced about three times as much acid as in the case of dry toluene. About 70% of the acid was benzoic, and about 30% formic. Radiation for 22 hours with ultraviolet light produced a little less acid than the two years of penetrating radiation. The products consisted of 44% benzoic, 36% formic and 20% oxalic acid."

The mathematics of the kinetics of radium emanation is a bit unexpected, p. 103. "The interaction of hydrogen and oxygen mixed with radium emanation can come to an end through the approximate exhaustion either of the emanation or of the gaseous mixture being acted on; the latter takes place in small bulbs with high emanation, the former in large bulbs. The actual pressure

(P) at any time t (or after decay of all emanation) may be calculated for any given case from the equation:

$$(\log P/P_0)/(E_0\ (e^{\lambda-t}-1))=84.1/D^2$$

"Contrary to the opinion expressed by some authorities, the ratio of quantity of emanation to quantity of reacting gas is not important from the kinetic standpoint. The ratio of emanation to reacting gases may rise continuously, as is the case in small volumes where the gases react at a faster percentage rate than the emanation decays, may pass through a maximum as in 3 cm spheres with about 100 millicuries of emanation, or may fall continuously, as in larger spheres, without affecting the velocity constant. This shows that, while the ratio of emanation to gas influences greatly the actual velocity of reaction, it does not change the value of $k\mu/\lambda$, thus proving that the general kinetic equation proposed holds, regardless of the relative concentrations, except as provided for in the equation."

The chemical effects of β and γ rays are so minute for nearly all gas reactions that a direct comparison of ionization and chemical action has not been possible in a strictly quantitative sense. The relative ionization produced by γ rays is of the order of 1/10000 of that of the corresponding α radiation, p. 113. "The most careful comparison of α and β-γ ray effects has been made by Usher. Using emanation in a glass capillary tube of 0.17 mm thickness, 0.208 cc of electrolytic gas was produced by the action of the penetrating radiation from 0.067 mm^3 of emanation in one month while the combined action of the α and penetrating radiation from 0.025 mm^3 of emanation till completely disintegrated gave a total of 5.840 cc of electrolytic gas (including H_2 from some H_2O_2 formation). Reduced to the same quantities of emanation, the joint effect of the rays is seen to be about 75 times as great as that of the penetrating rays alone, or the effect of the latter is about 1.3% of the combined effect. This is about what one should expect from the relative ionizations or kinetic energies. This appears to be strong evidence in favor of the same relationship between ionization and chemical action as that which has been shown to exist for α rays."

In nearly all the reactions brought about by α rays that have been investigated, there is an approximate statistical agreement between the number of ions generated (N) and the number of molecules acted upon (M). This appears to be true to the same degree of approximation both in gaseous and liquid systems, p. 115. The M/N ratio varies in the different reactions from about 0.5 to about 4.0. "An agreement within these limits for such a variety of reactions proceeding both with and opposed to the chemical free energy in both liquid and gaseous systems, when the disagreement might have been many million fold in either direction, appears to have fundamental significance and to warrant the application of a modified form of Faraday's Law to these reactions."

No such relation holds for the reaction between hydrogen and chlorine gases. Lind estimated that, for the penetrating rays, the M/N ratio exceeded unity by 100 to 1000 fold, p. 119. "This exceptional ratio led Bodenstein and Taylor to determine the effect of α rays on the same reaction. It was found that the reactivity of the mixture varied with its purity, as in the case of the photo-reaction, and that in the mixture of maximum sensitiveness at least 4000 molecules of H_2 and Cl_2 combine for one pair of ions formed. As will be shown in the following chapter, Bodenstein calculated that the rate of the photochem-

ical interaction of H_2 and Cl_2 exceeds the predictions of Einstein's photochemical equivalence law by a factor of about 10^6. Bodenstein was led to propose an electronic theory for photochemical action according to which an electron primarily liberated by any form of radiation can successively activate a large number of chlorine molecules, which then react with hydrogen, again liberating the electron at the time of reaction. This process would continue indefinitely from even a small number of initial free electrons except for the fact that finally the electron activates a foreign molecule (Chapman's inhibitors) and is not again liberated by the reaction. Bodenstein assumed oxygen to be the inhibitor in this case and that the ozone formed again decomposes to give oxygen. This fits with a number of other observations, namely, the inhibitive effect of oxygen and ozone actually observed by Chapman and MacMahon, and with the observation of Lind that ozone formation is statistically equivalent to the ionization, from which it follows that the free electrons are consumed in the reaction. It also explains why the reaction does not proceed after cessation of the radiation. As will be seen later, Bodenstein had to abandon the theory as applied to photochemical action of chlorine gas on account of the lack of ionization which he had assumed; but in the case of the action as produced by α particles where we have actual ionization, his theory remains applicable, in principle at least, to explain the abnormally high value of the M/N ratio. As alternative theories we shall have that of Nernst for the photochemical interaction H_2+Cl_2 and the later one of Bodenstein, both of which will be presented in the following chapter. The fact that the H_2+Br_2 mixture at ordinary temperature is not photo-sensitive and that its M/N value for α radiation is normal is of much interest."

In the case of the silent discharge, there is nothing analogous to Faraday's Law, p. 124. "Under some conditions Warburg found that about one thousand fold as much ozone is formed as would correspond to the current, or that instead of the theoretical 96,500 coulombs required per chemical equivalent, less than 100 coulombs suffice for the production of one gram-equivalent of ozone. Hitherto it has not been possible to confirm the theory that the total ozone formation would be accounted for by the ionization by electronic shock, because we have no means of measuring the total ionization produced. Conversely the conditions under which ionization by shock have been measured are not suitable for the formation and measurement of ozone."

The explanation for this seems to be that "ozone formation in gaseous oxygen is the result of the primary ionization of oxygen by some form of electronic discharge. The quantity of ionization involved in the ozone formation is not related directly to the flow of current, but is the far greater number of ions produced in the gas by electronic shock, which never reach the electrodes and therefore take no part in the electrical conduction, since the intensity of ionization far exceeds the limiting conditions for attaining saturation current.

Kirkby finds that the rate of reaction of oxyhydrogen gas under the influence of the electric discharge is proportional to the current passing and that about four molecules of water are formed per pair of ions, p. 125. Kirkby concluded that hydrogen molecules react with uncharged oxygen atoms, which are dissociated by collision with electrons under certain conditions. Only one-half of the collisions of electrons with the necessary velocity actually results in the dissociation of the oxygen molecule. Duane and Scheuer conclude,

p. 88, that α rays decompose water into hydrogen and oxygen, and that hydrogen peroxide is formed to some extent by the secondary action of nascent oxygen on water. At $-183°$ hydrogen and oxygen are formed in the proper ratio from ice, apparently because nascent oxygen cannot convert ice at that temperature into hydrogen peroxide.

Nernst considers that the photochemical reaction between hydrogen and chlorine is due to the formation of free chlorine atoms under the influence of light, p. 141. "The heat of reaction shows that the combination of a Cl atom with a H_2 molecule and the subsequent splitting of this unstable product to HCl and a free H atom take place with a large heat evolution, and therefore in the direction of spontaneous reaction according to the chemical free energy. Moreover, when a free H atom (just produced by the foregoing reaction) unites with a Cl_2 molecule we again have a reaction of the same nature. The Cl atom liberated by the latter reaction brings us back to the original system, and a cycle has been completed which may repeat itself indefinitely, except for the cross reaction of H and Cl atoms, and for the inhibitive effect of oxygen, which is assumed to remove the free Cl atoms from the field of action. By this purely thermodynamic method Nernst explains the multiplied secondary reaction in a mixture of H_2 and Cl_2, which accounts for the large departure from Einstein's law through the action of free atoms. In further support of the theory, Nernst calculates that a similar continuous cycle in the case of hydrogen and bromine is impossible, because one of the steps, $Br+H_2$, would not proceed spontaneously on account of a negative heat of reaction,—15,000 cals. And of course it is well known that a mixture of H_2+Br_2 is not light-sensitive at ordinary temperature. The further application of this or similar mechanisms to explain other cases of excessive action has not been attempted, but it is not without interest to note that in the only other two cases where the M/N value is as high as 10^6, we have halide and hydrogen present in the system." *Wilder D. Bancroft*

The Electronic Conception of Valence and the Constitution of Benzene. *By Harry Shipley Fry. 23 × 15 cm; pp. xviii + 300. New York: Longmans, Green and Co., 1921. Price: $5.00.*—The difference between the electronic structure formula and the ordinary one is that in the former, one end of the bond is positive and the other end is negative, while in the latter both ends are the same. On this basis the electronic formula can of course account for almost everything that the other can and for a lot of other things to boot. It contains the explicit assumption however, that all bonds are electrical and polar. Since that has not been proved, the value of the electronic conception of valence depends upon its usefulness. There is a very great difference between applicability and usefulness, a difference which the author does not always keep in mind.

The book is divided into four parts: the electronic conception of valence; the electronic formula of benzene; physical properties and physico-chemical phenomena; metal-ammines, bibliographical review, and general conclusions.

If all bonds are polar, then molecular hydrogen must contain one positive and one negative hydrogen atom. The author believes that negative hydrogen ions may be formed by electrolysis, p. 15. A hydrogen ion carrying a unit positive charge may lose it on contact with the cathode. The resultant neutral atom

immediately acquiring an electron from the cathode becomes a negative hydrogen ion which is naturally repelled from the cathode and immediately combines with an approaching positive hydrogen ion to form a molecule of hydrogen. An analogous and simultaneous process may be considered as taking place at the anode, in which case the negative chlorine ion gives up one electron to the anode, thereby becoming a neutral atom, which through the loss of another electron becomes a positive chlorine atom. The union of a positive and negative chlorine ion yields the molecule of chlorine.

This is a perfectly possible hypothesis; but is it true? That is a point which apparently does not interest the author. He had a wonderful chance to discuss nascent hydrogen and to show that his view did or did not account for the perplexing phenomena of over-voltage. He refuses to avail himself of it. Perhaps he does not know about nascent hydrogen and over-voltage; but even then, some friend should have called his attention to the omission. The explanation of the evolution of oxygen at the anode during the electrolysis of dilute hydrochloric acid solutions, p. 31, is not satisfactory because it postulates an irreversibility for which there is no experimental evidence.

On p. 23 the author states that the formation of sodium formate from sodium hydride and carbon dioxide is further evidence that the hydrogen of sodium hydride functions negatively; but the proof is far from being convincing. On p. 66 the author remarks parenthetically that chlorocarbonic ethyl ester is very frequently, but incorrectly called chloroformic ethyl ester, which implies that it is a derivative of formic acid. The reviewer had supposed that it could be made from formic acid which would make it a derivative in ordinary parlance of formic acid. It is tantalizing the way the author stops there. One would have liked to have him go on and predict the different effect of ferric and aluminum oxides on what we apparently should not have called trichlormethylchlorformate. On p. 69 we are told that the nitro group is negative in nitrous acid but positive in nitric acid. Doubtless the author is right; but then one does not quite see how nitric and nitrous acids can coexist because we should expect the reaction.

$$H^{\cdot} + NO' + NO_2^{\cdot} + OH' = H_2O + N_2O_4.$$

Perhaps this is the reason why nitrous acid increases the attack of nitric acid on copper; but we are not given any details. We are not told how this point of view will assist us in studying the action of metals on nitric acid a problem which interests the reviewer considerably at present.

On p. 138 the author discusses the action of halogen carriers. He postulates that when stannous chloride changes to stannic chloride, one of the extra chlorines is positive and the other is negative. This may be so; but it is difficult for the sceptic to believe this and also to believe that all four chlorines are negative in the case of carbon tetrachloride. If the formula of ferric chloride is written Fe_2Cl_6, then one of the last two chlorines is positive according to the author; but he does not tell us what would happen in case the formula were written 2 $FeCl_3$. In his discussion he states that phosphorus pentachloride behaves like antimony trichloride and he implies that sulphur chloride also does. The author says that the reviewer's guess that positive chlorine substitutes in the toluene side chain is wrong because the chlorine in benzyl chloride is negative as shown by hydrolysis tests. The conclusion may be right but the rea-

soning is not. When hydrogen reacts with chlorine, we must assume that the positive hydrogen reacts with the negative chlorine and the negative hydrogen with the positive chlorine; but nobody believes that we get two hydrochloric acids.

On p. 238 the author formulates the general hypothesis that "a substance manifests fluorescence whenever within the systems of dynamic equilibria of its electromers the number of diplex double bonds undergoing rearrangement is unequal to the number of contraplex double bonds simultaneously undergoing rearrangement." It seems perfectly hopeless when a man thinks that a statement like that is helpful. The author apparently believes, p. 245, that tabulating schemes of dynamic equilibria demonstrates "the existence of fluorescent transitions within the phasotropic equilibria of the electromers of anthracene and phenanthrene."

The important thing about the author's electronic theory of benzene is that he assumes the presence of three positive hydrogen atoms and three negative hydrogen atoms. Granted that, he is apparently able to predict, p. 52, that chlorobenzene on nitration will yield only ortho- and para-chlornitro-benzenes, while nitrobenzene, on chlorination, yields only meta-chlornitro-benzene. This is his one great point and about his only one.

It has been mentioned that he assumes explicitly that all bonds are polar. He also assumes less explicitly that all reactions are preceded by dissociation and are therefore ionic reactions. He quotes approvingly, p. 57, the statement by W. A. Noyes that "if we suppose what seems to be not improbable, that all reactions involving the decomposition of molecules are preceded by an ionization of the parts of the molecules, it would follow that elementary molecules as well may ionize into positive and negative parts."

He makes no use of contravalences and he ignores the possibility of addition reactions. His theory is therefore hopelessly one-sided. Mr. Fry is not convincing and he seems to lack all conception of what constitutes proof in the minds of others. When somebody later develops a real electronic theory of valence, it is probable that Mr. Fry will never understand why his pioneer efforts receive so little recognition. This book is a striking instance of a man having a really first-class idea but not being able to do anything with it *Wilder D. Bancroft*

Practical Chemistry. *By N. H. Black and J. B. Conant. 19 × 13 cm; pp. X + 474. New York: The Macmillan Co., 1920. Price: $2.00.*—In the preface the authors say: "Chemistry is so closely connected with many phases of modern life that almost everyone should have some knowledge of it. Its application to the problems of industry and recently to those of warfare has attracted unusual attention and interest. It pays no less important a part in the sciences of agriculture and medicine. For these reasons we believe that a knowledge of the fundamental facts of chemistry and an ability to use them should form a part of the equipment of our American youth.

"It is generally conceded that in order to teach any subject effectively it is first necessary to arouse an interest in it. Fortunately this is an easy task in chemistry if the method of presenting the subject is not too formal and academic. We have found two ways of awakening the student's interest: first, by appealing

to his love of the miraculous and dramatic; and second, by touching his curiosity concerning the things of every-day life."

This is admirable and the authors have carried out their plan well. On the very first page we find references to the souring of milk, the explosion of gasolene in an automobile cylinder, and the sudden burning of a flash-light powder. Further on are references to boiled eggs, lemonade, spontaneous combustion of oiled rags, lighting a fire, bacteria in drinking water, the kitchen stove, the thermos bottle, helium in balloons, ventilation, irrigation, solid alcohol, vulcanized rubber, fountain pens, refrigeration, gunpowder, coal and graphite, tarred roads, water gas, baking powder, fruit esters, washing with soap, dyes, sugar, paper, salt, fertilizer, matches, glass, aluminum, pottery, stalactites, plaster, iron and steel, electric furnaces, ink, photography, etc.

Good as this is the reviewer hopes that the authors will look upon this as a stepping-stone to something better. They have had to keep in mind the requirements of the College Entrance Examination Board, which means that they are hampered by the fact that the students must pass the regular examinations intended for those who are presumably going to take more chemistry. The reviewer would like to see the authors cut loose from this restraint and write a book for use in colleges and for people who intend to become tired business men and who do not intend to take any more chemistry.

The teaching of chemistry in the universities is done very well for those who intend to become chemists, engineers, or medical men; but there is no provision made for the man who would like to know something about chemistry as a part of a general education and not with the expectation of doing anything with it. The university has two functions: to train specialists, and to give a general education. The first is handled fairly satisfactorily; but the chemists do nothing at all in regard to the second. If the proper sort of a popular course in chemistry were given, it would be taken by a thousand students just as is now the case in some of the large history courses. The first university to take up seriously the question of giving general education courses all along the line will gain a great reputation. At present the field is practically untouched.

There are one or two points in which the book could be improved. It is perfectly true, p. 89, that we no longer consider night air as injurious; but our predecessors were not as stupid as one might think. The mosquito, which carries malaria, flies chiefly by night. The danger was not the night air but what came with it. Faraday did a good deal of work to overthrow the view expressed on p. 170 that the cathode attracts the positive ions and repels the negative ions. The war has been over long enough for the authors to have mentioned, p. 74, the use of special masks against carbon monoxide instead of the cumbrous oxygen helmets. Under the coagulation of casein in milk by acetic acid, p. 163, a specific reference to cottage cheese would have been appropriate. On p. 296 it is rather an over-statement to say that chemically pure salt does not absorb water from air. In very damp weather any salt will form lumps.

Wilder D. Bancroft

A STUDY OF THE SYSTEM AMMONIA-WATER AS A BASIS FOR A THEORY OF THE SOLUTION OF GASES IN LIQUIDS[1]

BY BENJAMIN S. NEUHAUSEN AND W. A. PATRICK

Introduction

To a great extent the aim of most investigations on the absorption of gases in water and other liquids has been to note how far the particular gas conformed with, or deviated from Henry's law. The investigation of the absorption of gases by liquids may be said to begin with Henry's[2] study of the absorption of carbon dioxide by water, a result of which was his famous law that the quantity of a gas absorbed in a liquid is proportional to the pressure of the gas. Dalton's theoretical explanation of this law on the basis of Boyle's law, and his equally well known law of partial pressures of gases[3] tended to give a very definite trend to the problem of absorption of gases by liquids.

Through the investigations of Bunsen[4] on the absorption of the fixed gases, of Schonfeld[5] on hydrogen sulphide, of Roscoe and Dittmar[6] on ammonia and hydrochloric acid, and of Sims[7] on ammonia and sulphur dioxide, it became evident that Bunsen was correct in his stand that the general law that expresses the relation between pressure and the quantity of gas absorbed is a complex function and that conformity to Henry's law in case of the relatively soluble gases was the exception rather than the rule. It was also recognized that the chemical properties of the molecules involved, as for instance their attraction for one another influenced markedly the absorption.

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[1] Contribution from the Chemical Laboratory of Johns Hopkins University.

[2] Phil. Trans., 1803; Gilb. Ann., **20**, 147 (1805).

[3] Gilb. Ann., **12**, 385 (1803).

[4] Liebig's Ann., **93**, 1 (1855).

[5] Ibid., **95**, 1 (1855).

[6] Ibid., **112**, 327 (1859).

[7] Ibid., **118**, 333 (1861).

Thus, for example, Roscoe and Dittmar differentiate clearly in their investigation between the absorption of hydrochloric acid gas and ammonia, since a current of air passed through an aqueous solution of hydrochloric acid can only remove gas up to a definite concentration while all the ammonia may be removed from an ammonia solution. This tendency to account for absorption of gases on the basis of physical and chemical properties had its first advocate in Th. Graham[1] who in a very remarkable paper advanced the theory that gases were actually condensed when they were absorbed by a liquid, and that solutions of gases should be considered as binary liquid mixtures of the solvent and liquefied gas. To this view we shall return in the discussion of the results.

The interest as to the validity of Henry's law did not cease, and a number of investigations on the solubility of carbon dioxide were pursued. While Khanikoff and Louguinine[2] found that Henry's law held up to four atmospheres, v. Wroblewski,[3] Cassuto,[4] and Sander[5] found that there was a marked deviation up to 100 C.

Ammonia was chosen for the present investigation for a number of reasons. First, it has a very high solubility in water that changes very markedly with the pressure, and thus there are avoided those slight absolute changes in solubility in the case of a gas as carbon dioxide, in the interpretation of which free rein is given to preconceived notions. Secondly, because of its economic importance, the physical constants of ammonia, such as vapor tensions, density of the liquid, surface tension, etc., have been determined more accurately than most other gases. Thirdly, it has a relatively high critical temperature.

The first investigator to work extensively on the absorp-

[1] Annals of Philosophy, **12**, 69–74 (1826); Chemical and Physical Researches (Edinburgh, 1876), pp. 1–6.

[2] Ann. Chim. Phys., (4), **11**, 412 (1867).

[3] Wied. Ann., **17**, 103 (1882); **18**, 290 (1883).

[4] Nuovo Cimento, (5), **6**, (1903).

[5] Zeit. phys. Chem., **78**, 513 (1912).

tion of ammonia was Carius.[1] His methods and results were proved unreliable by Roscoe and Dittmar[2] who investigated the absorption of ammonia by water up to a pressure of 2000 millimetres, at 0° C. Sims[3] checked their values and investigated the absorption also at 20° C and 40° C up to 2100 millimetres, and at 100° C up to 1400 millimetres. Watts[4] also obtained results in agreement with Sims, while Raoult[5] who worked at one atmosphere and varying temperatures obtained somewhat higher values than the other investigators. Perman[6] who worked at 0° C, 20° C, and 40° C, with solutions up to 22.5% obtained vapor pressures that tally fairly well with those of Sims. Mallet[7] working at a pressure of 743–744.5 millimetres obtained the solubilities at −10° C, −20° C, −30° C, and −40° C.

I. The Investigation of the Vapor Phase.

1. Apparatus

The composition of the vapor phase of binary liquid mixtures has been studied both by dynamic and static methods. The principal dynamic method was to allow the liquid mixture to boil at certain pressures and temperatures and to analyze the distillate and residue by a refractometer, as for example, in the classical researches of Zawidzki;[8] or to bubble air through the solution and absorb the vapors in suitable solutions, and thus determine the composition of the vapors, as was done, for instance, by Perman[9] in his research on the vapor pressures of ammonia solutions. Both of these dynamic methods are open to rather grave objections. First, in order to have the vapor, collected as distillate or in suitable solutions, correspond with any degree of accuracy to the solution of the composition

[1] Liebig's Ann., **99**, 129 (1856).

[2] Loc. cit.

[3] Loc. cit.

[4] Liebig's Ann. Suppl., **3**, 227 (1864).

[5] Ann. Chim. Phys., (5), **1**, 262 (1874).

[6] Jour. Chem. Soc., **79**, 718 (1901); **83**, 1168 (1903).

[7] Am. Chem. Jour., **19**, 804 (1897).

[8] Zeit. phys. Chem., **35**, 129 (1900).

[9] Jour. Chem. Soc., **83**, 1168 (1903).

at the beginning or the end of the experiment, one has to begin with a large volume of liquid; and moreover one must distill off only a small portion. Especially in cases in which one of the components has a high vapor pressure, the process should be continued for only a short time. It is very questionable, as Roozeboom[1] observes, whether in mixtures, in which there is a great difference in the composition of both phases, whether the vapor that is formed at the first few minutes corresponds to the true equilibrium. In fact, impelled by such considerations, Cunaeus[2] preferred to let the vapor remain in contact with the liquid and analyzed the same by optical methods. Moreover, as in the present investigation, solutions of high concentrations of ammonia were used, and the total vapor pressure of the solution is most often more than one atmosphere even at 0° C, distillation consequently was made rather difficult. As for the bubbling method, its disadvantages have already been expressed by Perman:[3] "Unfortunately, the method is not applicable over a very wide range of temperature or with very varying concentrations of the solution, for when the vapor pressure becomes nearly equal to atmospheric pressure, a very little air will draw off a large quantity of vapor, and moreover evaporation of ammonia becomes so rapid, that it is impossible to keep the temperature constant." Another obstacle to the use of any dynamic method for this investigation, can be seen from one of the results obtained at 0° C. An ammonia solution which has a partial pressure of 1868 mm ammonia at 0° C, has a partial pressure of 0.51 mm of water. Now assuming ammonia to obey the ideal gas laws, to obtain even 5 mg of water, 22.8 litres of vapor reduced to standard conditions, or practically one gram mole of ammonia would have to be distilled off, a volume too large to deal with, and moreover, a huge quantity of solution would be required in order to be able to neglect the loss of that much ammonia.

[1] Heterogene Gleichgewichte, II, part I, page 20.
[2] Zeit. phys. Chem., **36**, 232 (1901).
[3] Loc. cit.

A static method for measuring partial pressures was therefore developed on the basis of the following considerations.

At a fixed temperature, a solution of a certain definite composition of A and B, has a fixed total pressure, made up of two well defined partial pressures of the vapors of A and B. B is assumed to have a greater vapor pressure than A. Now, suppose that by some means a quantity of vapor of A is forced into the vapor phase of the system. Since the partial pressure for A is exceeded, some of it will condense. As some of the vapor of B will also dissolve in this condensate, a re-adjustment will take place, and a solution will be obtained which is somewhat less concentrated with respect to B, and since B has been assumed to have a much greater pressure than A (in the present case, on the order of the relative vapor pressures of ammonia and water), the partial pressure of B is appreciably diminished, while that of A is slightly increased. The system therefore will suffer a lowering in the total pressure, since the volume is not changed appreciably by the minute quantity of condensate.

This idea was then extended as follows: If to ammonia gas at a certain temperature and pressure below that corresponding to the vapor tension of liquid ammonia at that temperature, there is gradually added some water vapor, the pressure of the mixture will rise until the partial pressure of the water vapor equals that corresponding to the partial pressure of water vapor over a solution whose partial pressure of ammonia at that temperature is such as at the start. Any further addition of water vapor will entail condensation of water with consequent solution of some ammonia and reduction in the total pressure.

In Fig. 1 is given a sketch of the apparatus employed. By opening reducing valves R_1, R_2, R_3, and R_4, ammonia passed in from the ammonia tank into the manometer and small wrought iron tanks T_1 and T_2. The auxiliary manometer (A M) was bent at an obtuse angle of 157 degrees so that angle "a" had a sine of .1994. Thus a rise or drop of one

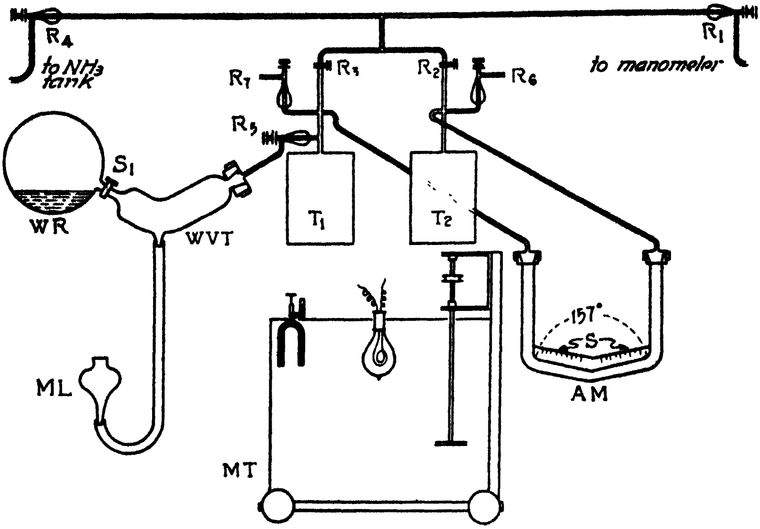

Fig. 1

millimetre in the vertical would be indicated by a rise or drop of five millimetres of the mercury in the oblique tubing and could be read on the attached scale "S" to within 0.2 mm. In other words, change of pressure in tank T_1, from that of tank T_2 could be measured to 0.08 mm. When we consider that Perman[1] only claimed an accuracy of 0.5 mm for his measurements of the partial pressure of water vapor in total pressures up to 600 mm, the advantage of this static method can be seen.

The water vapor was injected by means of the water vapor injector (W V I) which was connected by means of valve R_5 to T_1. The distilled water contained in the reservoir bulb (W R) was allowed to distill over into W V I which was evacuated in the following manner. Valves R_2 and R_3 were closed to prevent any direct communication between T_1 and T_2, while R_5 was opened. Exhaust valves R_6 and R_7 were connected by a "Y" tube to a vacuum pump and evacuated. That was continued intermittently for several hours while

[1] Loc. cit.

S_1 was shut and opened at intervals. R_5 and S_1 were then shut off, and ammonia was passed into T_1 and T_2 through R_2 and R_3 and these tanks were then evacuated. This process was repeated a number of times in order to remove any water vapor remaining in T_1. By opening R_5 and raising the mercury level bulb (M L) the vapor could be forced into T_1.

M T was a movable thermostat that could be raised and lowered by means of pulley and tackle. The temperature was regulated to 0.05° C. It was necessary to have this movable thermostat in order to be able to remove it, when the ammonia in T_1 and T_2 had to be cooled by means of a mixture of carbon dioxide snow and ether before the water vapor could be forced in.

All the tubing used in the apparatus was made of brass. The metal-glass joint between the water vapor injector and R_5 is described further in this account.

The pressure was measured by means of a continuous open mercury manometer, which consisted of four glass U-tubes, each having a length of 1600 mm. These were of hard glass with a 6-mm bore and a wall thickness of 1 mm. It is diagrammatically represented in Fig. 2. The structure

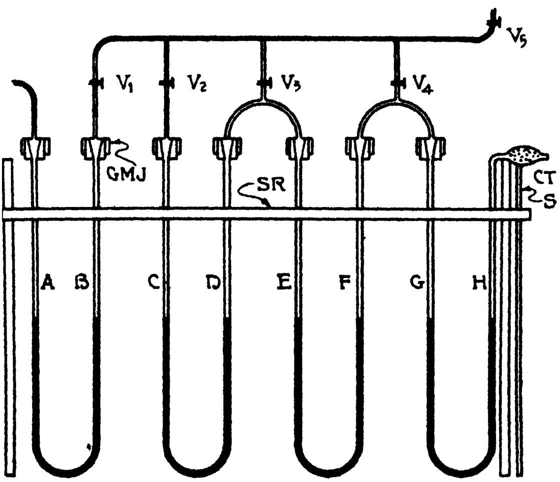

Fig. 2

into which the glass U-tubes were mounted was made of brass tubing, and the glass tubes were connected to it by means of glass-metal joints (G M J) described below. The U-tubes were filled half their length with redistilled mercury, and all the space from the top of the mercury in "B" to the mercury in "G," including the metal structure, was filled with benzene, which was used as the communicating liquid. "H" communicated with the air through a tube filled with soda lime. Since each tube was 1600 mm in length, a total pressure of 8 atmospheres, after making various corrections, plus the corrected barometric reading at the time, could be measured, or approximately 9 atmospheres. Readings were made to the nearest millimetre, so that the maximum error in reading, when all the U-tubes were in series, could be about 4 mm, and there was correspondingly less error as fewer tubes were read. A sliding rod "S R" that could slide over two fixed posts was used to read differences in level between the mercury columns. As can be seen from the diagram, there was no need for correction for meniscus depression. Valves V_1 and V_2 were always open. By keeping valves V_3 and V_4 closed the pressure was measured by the whole series. By opening V_3 the second U-tube was by-passed and by opening both V_3 and V_4 both the second and third U-tubes were by-passed. V_5 was used as an exhaust valve.

The idea of a continuous manometer was first applied by Richards in 1845. Thiesen[1] and then Wiebe[2] both discussed and described such manometers. By using compressed gas as the communicating fluid, H. Kamerlingh Onnes[3] had found such an arrangement very satisfactory in making high pressure measurements, in which greater accuracy was desired than is obtainable with a closed gas manometer. Recently at the Bureau of Standards,[4] such a manometer was used to measure pressures up to 15 atmospheres with success,

[1] Zeit. Instrumentenkunde, **1881**, p. 114.

[2] Zeit. comprimierte Gase, **1897–1898**, pp. 8, 25, 81, 107.

[3] Communications Phys. Lab. Leyden, Nos. 44, 67, 70 and 146.

[4] Jour. Am. Chem. Soc., **42**, 206 (1920).

alcohol being used as the communicating liquid. The improvement made in the manometer used in the present work was that the U-tubes were all of practically like bore, and so pressure could be read at any point desired, while in those used at Leyden and at the Bureau of Standards, the tubes were of very small bore with the exception of a small section in the lower part of the left arm and in the upper part of the right arm. Because of this restriction there was much additional manipulation and balancing necessary, and pressures less than a given pressure could not be measured. While the arrangement used in this investigation required a greater quantity of mercury, yet this disadvantage was thought to be overbalanced by the considerations noted above.

Fig. 3 illustrates the method employed in making glass-metal joints. The tubing which it was desired to connect had a flange in it (F). There was a leather gasket on this flange (L_1). The glass tubing was flared and inserted in the metal collar (M C) and made fast with plaster of Paris, (P P). The glass surface was then polished in turn with rough and fine emery and rouge. A second leather gasket (L_2) was put between the collar and the flange, and the two were put firmly together by means of the nut (N) that slipped over the flange and screwed over the collar.

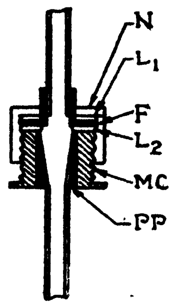

Fig. 3

The ammonia used in this work was obtained from the Goetz Ice Machine Co., Philadelphia, Pa., and was kept over metallic sodium to remove the water. The hydrogen that was generated was allowed to escape by allowing a quantity of ammonia to escape twice daily for a week, until absence of fixed gases was indicated by the fact that no gas remained behind after passing 500 cc of the gas through sulphuric acid. The ammonia which was to be used in the investigation of the vapor phase was then distilled into a second cylinder, the first and last fractions being discarded. In the experiments

on the solubility of ammonia, it was found unnecessary to make this distillation, since the ammonia so dried, showed no trace of fixed gases, and since before starting a run a large volume of ammonia was always run through the apparatus to remove any air.

The temperature of 0° C was obtained by mixing washed ice shavings with water; and those of 20° C and 40° C by means of an electric thermostat.

2. Procedure

In the investigation of the vapor phase, the following procedure was followed. Valves R_1, R_2, and R_3 were opened, and a vacuum pump connected with R_6 and R_7. After the system had been exhausted, R_6 and R_7 were shut off, and R_4 was gradually opened until there was a pressure of about two atmospheres of ammonia in the tanks. Valve R_4 was then shut off and the system again evacuated. This was repeated from six to ten times before every run. Ammonia was then allowed to come into the system. After standing in the thermostat for about half an hour, after which time the manometer did not indicate any change in the pressure, valves R_1, R_2, and R_3 were shut off. The continuous manometer as well as the barometer were then read and the temperature of the room was then noted. The thermostat was then lowered, and moved from under the tanks T_1 and T_2, and T_1 and T_2 were immersed in a mixture of carbon dioxide snow and ether, the ammonia in the tanks being cooled and the pressure reduced to 70–80 mm. The mercury level bulb was then raised and R_5 opened and a quantity of water vapor forced in. R_5 was then closed and T_1 and T_2 were immersed in a beaker of water of 60° C for about ten minutes, and then the thermostat was raised in place. After a half hour when the auxiliary manometer showed no further change in the drop of the mercury on the side connected to T_1, the drop was noted. This injection of the water was repeated from five to six times until the mercury in this side began to rise, indicating a drop in

pressure in T_1. The average between the last reading at which an increase in pressure was indicated and the first at which a decrease was noted, was considered as the partial pressure of the water vapor corresponding to that pressure of ammonia at the temperature of the thermostat. The data thus obtained were recalculated as shown in the following specimen record sheet:

Temperature of Bath: 20° C.

Height of mercury in B	1053 mm	
Height of mercury in A	213 mm	840 mm
Height of mercury in D	1049 mm	
Height of mercury in C	205 mm	844 mm
Height of mercury in F	1051 mm	
Height of mercury in E	213 mm	838 mm
Height of mercury in H	1102 mm	
Height of mercury in G	268 mm	834 mm

Total mercury height in manometer	3356 mm	
Room temperature near manometer	23.75 C	
Factor to correct for expansion of Hg	0.9956	
Therefore true height mercury column	3341.1 mm	
Corrected barometric reading	757.3 mm	
Therefore total corrected pressure of mercury	4098.4 mm	(R_1)
Length of benzene column in "B"	617 mm	(L_1)
Difference in length between benzene in C and D	939 mm	(L_2)
Difference in length between benzene in E and F	838 mm	(L_3)
Length of benzene column in G	1037 mm	(L_4)
Equivalence factor of benzene at 23.75 C to mercury at 0 C is	0.0643 (c)	
$(L_2 + L_3 + L_4 - L_1)$ c	159.1 mm	(R_2)
R_1 minus R_2 net ammonia pressure	3939.3 mm	
Reading on differential manometer	8.25 mm	(max.)
Reading on differential manometer	7.25 mm	(first drop)

$$\frac{8.25 + 7.25}{2} \times \frac{2}{5} = 3.1 \text{ mm partial pressure of water.}$$

3. Results

The results obtained are given in the following table:

TABLE I

Composition of the Vapor Phase of Aqueous Ammonia Solutions.

Temperature 0° C

Partial pressure of ammonia in mm	Partial pressure of water in mm
1062	1.04
1100	1.00
1334	0.84
1868	0.51
2078	0.35

Temperature 20° C

Partial pressure of ammonia in mm	Partial pressure of water in mm
1146	8.6
1288	8.3
1445	7.4
2113	5.9
2112	6.0
2647	4.5
2624	4.6
3563	3.7
3725	3.4
3942	3.1

Temperature 40° C

Partial pressure of ammonia in mm	Partial pressure of water in mm
1120	32.1
1389	29.8
1579	26.5
1582	26.4
1926	22.4
2132	20.8
2381	19.3
2546	18.9
2969	18.3
3053	18.3
3395	17.8
3957	17.4
3928	17.4

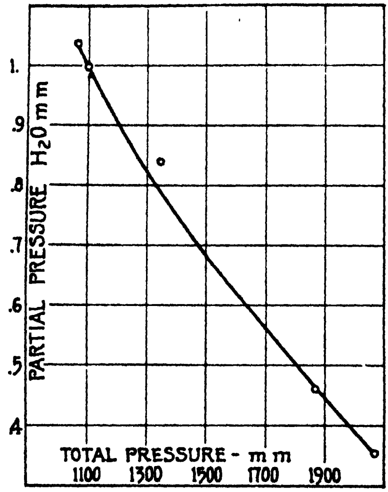

Fig. 4
Partial Pressure H_2O and Total Pressure
NH_3–H_2O System at 0° C

In Figs. 4 and 5 are plotted the partial pressures of water as ordinates and the total pressures of ammonia plus water as abscissae for 0° C, 20° C, and 40° C.

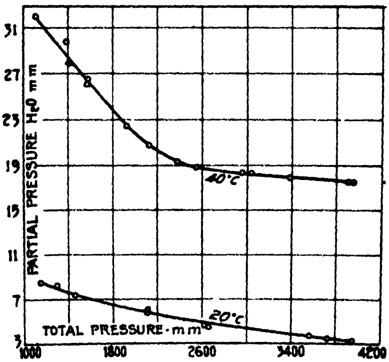

Fig. 5
Partial Pressure H_2O and Total Pressure
NH_3–H_2O System at 20° C and 40° C

II. Investigation of the Liquid Phase.

1. Apparatus

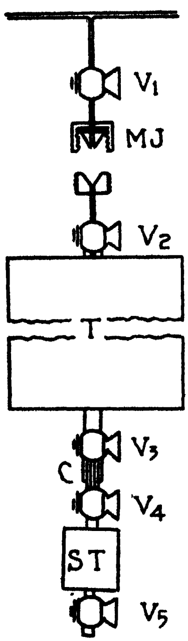

Fig. 6

In Fig. 6 is a sketch of the apparatus for determining the solubility of ammonia in water at different pressures at 0° C, 20° C, and 40° C.

T, the solubility tank of about 500 cc in capacity, was connected to the ammonia tank and to the manometer by means of the metal joint (M J), which as can be seen from the figure was similar in construction to the glass-metal joints. When it was desired to pass ammonia in or to measure the pressure of the gas phase, the connection by means of M J would be made, and valves V_1 and V_2 opened. A sample of the solution could be obtained in the small tank S T which unscrewed from T at C. An eccentric was used to shake the solution by causing the tank to make a 60-degree arc of a circle in the thermostat.

The temperature was regulated to 0.05° C.

The pressure was measured on the same manometer described above.

2. Procedure

The tank T, without the sample tank S T, was filled with water and connected to the cylinder of purified ammonia. By opening V_3 about 300 cc of water was displaced, and about 200 cc of water with an atmosphere of ammonia remained. The sample tank was now screwed on to T, V_3, V_4, and V_5 remaining shut and ammonia was allowed to pass in for ten minutes. The tank was then disconnected and shaken for about ten minutes, and then more ammonia was passed in. When, after this procedure had been repeated for a number of hours, the pressure reading reached a value about that desired;

no more ammonia was passed in, and shaking was continued for fifteen minutes at intervals, until pressure readings changed by only several millimetres, and equilibrium was then considered to have been reached. The pressure registered by the manometer, the barometer reading, and the temperature of the room were noted. V_5 was then connected to a vacuum pump, and V_4 and V_5 opened, and S T evacuated. V_5 was then closed and V_3 opened. The pressure above faced the solution into S T. After about a minute V_3 and V_4 were shut and S T unscrewed.

The above method of drawing off a sample was found not to affect the concentration of the solution by the increase of the vapor phase during the short time that the sample was withdrawn. For example, a second sample taken ten minutes later weighed only 8 mg more, and on analysis contained 1/10 of 1% less ammonia than the first sample. This method, moreover, had the advantage that equilibrium did not have to be reached through a small opening in the valve.

The sample tank was carefully dried with filter paper and weighed. The solution was then run into a measured quantity of standard sulphuric acid, the sample tank being thoroughly washed out. S T was dried by compressed air and weighed. Every third or fourth time, it was filled with mercury and weighed to determine the internal volume, so as to ascertain whether any change had taken place because of corrosion.

An aliquot part of the sulphuric acid solution was titrated with dilute sodium hydroxide solution, methyl red being used as the indicator. Thus the quantity of ammonia present was determined.

A sample record sheet of one solubility determination will illustrate the procedure:

Temperature of bath: 20° C

Height of mercury in B	727 mm	
Height of mercury in A	529 mm	198 mm
Height of mercury in H	767 mm	
Height of mercury in G	571 mm	196 mm

Total mercury height in manometer	394 mm
Room temperature near manometer	28 C
Factor to correct for expansion of mercury	0.9948
Therefore true height of mercury column	392 mm
Correct barometric reading	765 mm
Total corrected mercury height	1157 mm (R_1)
Difference in columns of benzene between G and B	156 mm (L)
Equivalence factor of benzene at 28° C to mercury at 0° C	0.0638 (c)
$L \times c = R_2$	10 mm
$R_1 - R_2$ = Total vapor pressure of solution	1147 mm
Weight of sample tank and solution	196.001 g
Weight of sample tank	186.195 g
Weight of solution	9.806 g
222.91 cc 1.0532 N H_2SO_4 neutralized	3.991 g NH_3
Water present in sample	5.815 g
Therefore 0.686 g NH_3 per gram water	
Weight sample tank and mercury at 24° C	339.835 g
Weight sample tank	186.195 g
Weight of mercury at 24° C	153.640 g
Therefore volume	11.35 cc
Therefore density of solution	0.864

Now by calculating from Berthoud's[1] values, the density of liquid ammonia at 0° C, 20° C, and 40° C, and from the density of water at these temperatures, there could be obtained the densities that the ammonia solutions would have if no contraction in volume of the water and ammonia had taken place. From these calculated values and densities found for the solutions, the contraction in volume could be calculated. Also, by means of curves in Figs. 4 and 5, the partial pressures of water vapor in the total pressures observed could be read off.

3. Results

In Table II the solubility data obtained is summarized.

Because of the very large difference in the vapor pressures of ammonia and water, it was impossible to plot the partial pressure curves of both the ammonia and water on one diagram. To be able to compare the relative trend of the two curves

[1] Helv. Chim. Acta, 1, 84–87 (1918).

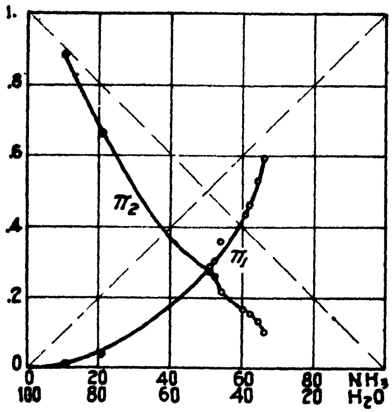

Fig. 7
Reduced Partial Pressure Curves of NH_3 and H_2O at 0° C

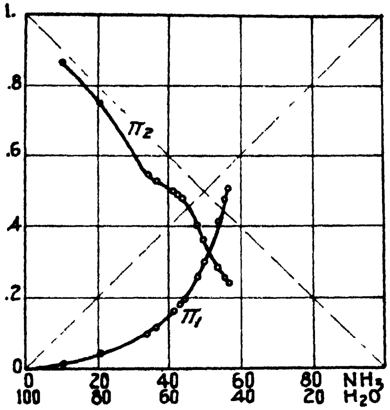

Fig. 8
Reduced Partial Pressure Curves of NH_3 and H_2O at 20° C

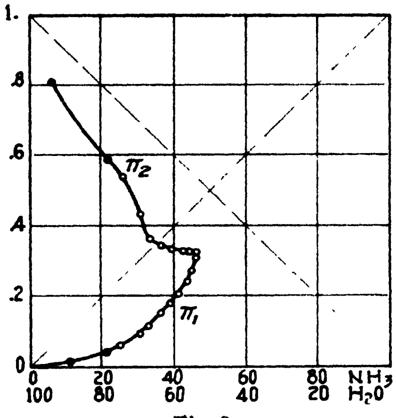

Fig. 9
Reduced Partial Pressure Curves of NH_3 and H_2O at 40° C

in one diagram, there have been plotted in Figs. 7, 8, and 9, the partial reduced pressures of the ammonia and water, for the various mole fractions of ammonia at 0° C, 20° C, and 40° C. The reduced partial pressures are the ratios between the observed partial pressures and the pressures of the pure components at these temperatures. π_1 and π_2 indicate the ammonia and water curves, respectively. Points marked with an X are taken from Perman's work.

TABLE II

Solubility of Ammonia in Water

Temp. C	Mole fraction % ammonia	Partial pressure of ammonia, mm	Calc. P. P. NH_3 by Raoult's Law	Partial pressure of water in mm	Calc. P. P. H_2O by Raoult's Law	Density solution	% Contraction in volume	K_1	K_2	K_3
0°.C	51.676	915	1664.5	1.25	2.208	0.842	7.50	1.1032	.5644	.4621
	52.382	944	1687.2	1.19	2.176	0.842	7.80	1.0002	.5547	.4543
	54.735	1140	1763.0	.97	2.068	0.833	7.80	1.0029	.4803	.3897
	61.206	1409	1971.4	.77	1.773	0.817	9.21	1.0582	.4345	.3470
	62.765	1499	2021.6	.708	1.701	0.812	8.52	1.0613	.4184	.3326
	65.076	1684	2096.1	.61	1.600	0.803	8.51	1.0451	.3465	.3041
	65.711	1732	2116.5	.545	1.567	0.800	8.35	1.0456	.3798	.2978
	66.621	1865	2145.9	.46	1.525	0.795	8.12	1.0106	.3572	.2785
20°	34.886	728	2242.6	9.4	11.304	0.882	7.07	0.6950	.4792	.4073
	36.508	798	2347.	9.25	11.025	0.878	7.25	0.6861	.4575	.3872
	42.077	1140	2705.	8.6	10.057	0.864	8.30	0.6017	.3691	.3084
	42.392	1165	2725.1	8.55	10.003	0.862	8.17	0.5965	.3636	.3031
	43.086	1226	2769.8	8.4	9.882	0.854	8.16	0.5832	.3515	.2905

TABLE II (*Continued*)

20° C	43.731	1281	2811.2	8.3	9.770	0.848	7.37	0.5730	.3414	.2802
	48.175	1677	3097.	7.05	8.839	0.845	8.96	0.5239	.2874	.2355
	49.941	1938	3213.4	6.33	8.692	0.835	8.36	0.4871	.2577	.2092
	53.940	2655	3467.5	5.1	7.997	0.825	9.47	0.4166	.2032	.1632
	55.970	3076	3598.	4.45	7.645	0.817	9.47	0.3903	.1819	.1449
	56.923	3277	3659.3	4.15	7.476	0.815	9.65	0.3808	.1737	.1381
40° C	25.011	752	2915.6	36.5	41.143	0.902	6.05	0.4192	.3328	.2875
	25.366	774	2957.2	36.2	40.949	0.9005	6.21	0.4147	.3277	.2893
	30.690	1134	3577.7	32.1	38.027	0.8833	7.21	0.3688	.2706	.2297
	32.686	1335	3810.4	29.5	36.933	0.817	7.68	0.3435	.2448	.2065
	33.134	1376	3862.6	29.0	36.692	0.8755	7.74	0.3401	.2414	.2029
	36.326	1787	4234.8	23.9	34.935	0.864	8.22	0.3018	.2033	.1693
	39.026	2180	4549.5	20.5	33.454	0.856	8.52	0.2773	.1791	.1480
	41.133	2460	4795.1	19.0	32.298	0.849	9.05	0.2676	.1668	.1365
	42.925	2832	5004.0	18.42	31.315	0 843	10.00	0.2508	.1516	.1236
	44.624	3226	5202.0	18.0	30.382	0.837	9.49	0.2359	.1383	.1121
	44.557	3214	5194.3	18.0	30.420	0.837	9.42	0.2361	.1386	.1123
	46.335	3640	5401.7	17.6	29.445	0.828	9.40	0.2240	.1273	.1022

K_1 equals 1000 times the ratio between grams of ammonia per gram of water and the equilibrium pressure of ammonia.

K_2 equals 10 times the ratio between mole fraction of ammonia and the equilibrium pressure of ammonia.

K_3 equals the number of grams of ammonia per litre of solution divided by the equilibrium pressure of ammonia.

Discussion of Results

From Figs. 7, 8, and 9, it is noted that the partial pressure curves of the ammonia are concave to the straight line curve of ideal mixtures, and that the curves tend to approach this line with increasing concentration of ammonia. This approach becomes more marked with increasing temperature. Whether these curves, if continued, would cut the straight line curve, and then become concave to the axis of abscissae (i. e., a negative-positive curve as in the pyridine–water system investigated by Zawidzki)[1] or whether the curve would approach the straight line and become asymptotic to it cannot be foreseen. Yet from analogy with the curves of the partial pressures of water it is very probable that the ammonia curves become asymptotic to the straight line; or, in other words, that in dilute solutions of water in ammonia, the partial pressures of the ammonia would approach those required by Raoult's Law.

From the curves of the partial pressures of the water, it is seen that the straight line is approached as the mole fraction of the water increases. As will be noted by comparison with Table II, the regions, in which flex points appear, correspond to those concentrations in which there is a maximum or minimum contraction in volume. Nothing further can be advanced at present to account for this phenomenon.

Since the vapor pressure of ammonia is so much greater than that of water, the total vapor pressure curve will be that of the ammonia curve, and therefore the ammonia solution will most probably not show a maximum or minimum boiling point, as had already been stated by Konowalow.[2]

A Theory of the Solution of Gases in Liquids

The fundamental concept of the theory of the solution of gases in liquids, which it is desired to advance, is that first enunciated by Graham[3] in his remarkable paper, namely

[1] Zeit. phys. Chem., **55**, 129 (1900).
[2] Ber. deutsch chem. Ges., **17**, 1531 (1884).
[3] Loc. cit.

that "gases owe their absorption by liquids to their capability of being liquefied and to the affinities of liquids to which they become in this way exposed," and that "solutions of gases in liquids are mixtures of a more volatile with a less volatile liquid." Since the condensation of the gas is regarded as the fundamental phenomenon of its absorption by a liquid, and solutions of gases in liquids are liquid mixtures, the following postulates follow:

1. A gas cannot be dissolved in appreciable quantities above its critical temperature, since above the critical temperature liquefaction is impossible. The fixed gases are dissolved to some extent by water and other liquids, but if absorption coefficients are discarded, and the relative number of gas molecules dissolved by the water molecules considered instead, the exceedingly small quantity becomes apparent. Thus according to v. Antropoff[1] one gram of water absorbs 0.123 cc Xenon reduced to N. T. P., Xenon being the most soluble of the noble gases. In other words, 0.055 of a gram mole of water absorbs 0.0_555 of a gram mole of Xenon, or one molecule of Xenon for 10,000 molecules of water. It is not true liquefaction that is taking place in such cases, but rather a retention of the Xenon molecule by the attractive forces of numerous water molecules.

2. Since solutions of gases in liquids are to be considered as liquid mixtures, the degree of miscibility of the liquids are of great importance. Thus, since liquid carbon dioxide and liquid sulphur dioxide have only a limited miscibility with water, their gases should dissolve in water to a limited extent, for any liquefied gas separating out could not remain as such except at a partial pressure equal to its vapor tension at that temperature. The relative size and shape of the pores in the liquid would also tend to influence the quantity of gas dissolved. Thus Just[2] found that the solubility of carbon dioxide in various liquids was greater the smaller the refractive index.

[1] Zeit. Elektrochemie, **25**, 269 (1919).
[2] Zeit. phys. Chem., **37**, 343 (1901).

This phenomenon could be explained on the basis of the Clausius-Mossotti formula and the electro-magnetic theory of light, whereby

$$u = \frac{n^2 - 1}{n^2 + 2}$$

in which u is the true space occupied by the molecules and n is the refractive index. Likewise, solubility might be in some way related to a quantity such as "b" of van der Waals.

3. The chemical nature of the gas molecules, such as polarity would likewise influence the degree of solution. This was already recognized by Roscoe and Dittmar[1] in their investigation of the solubilities of ammonia and hydrogen chloride in water. Thus, while they denied Bineau's contention that the constant boiling mixtures of hydrochloric acid were definite compounds, they nevertheless concluded that between water and hydrochloric acid there is an attraction appreciably different from that with other gases. The other inorganic acids forming constant boiling mixtures are also strongly polar substances.

On the basis of the above considerations, the solution of gases in liquids may be classified, as follows:

I. Solution of gases above their critical temperature.

II. Solution of gases below their critical temperature.

(1) Gases, whose condensates have limited miscibility with water, and which are only limitedly soluble, e. g., CO_2 and SO_2.

(2) Gases, whose condensates are miscible with water in all proportions,

(*a*) Those of strong polarity which form constant boiling mixtures, as HCl, and are extremely soluble.

(*b*) Those whose polarity is not as strong, as NH_3, which can be driven entirely out of solution.

Patrick and McGavack[2] in their theoretical discussion of

[1] Loc. cit.

[2] Jour. Am. Chem. Soc., **42**, 946 (1920).

the results obtained in their investigation of the adsorption of sulphur dioxide by silica gel, attacked the problem of adsorption in the following manner. Postulating that when any gas is adsorbed in appreciable quantity, condensation of the gas is actually taking place, the question arises how one can account for the fact that the gas pressures in equilibrium are much lower than the vapor tension of the liquefied gas. These authors on the basis of capillarity advanced the thesis that the lowering of the vapor pressure was due to the fact that the liquid was under a tension or a negative pressure. It is well known that a liquid under a hydrostatic pressure has a greater vapor pressure than when under the pressure of merely its own vapor, and conversely when it is under a tension or negative pressure, one would expect a lowering in the vapor pressure. This tension could be calculated on the basis of the Gibbs' relation

$$\left(\frac{dp}{dP}\right)_T = \frac{V}{v},$$

in which dp equals the change in vapor pressure, dP equals change in hydrostatic pressure, V equals volume of condensed liquid phase, and v equals volume of the gas. Furthermore, this tension must cause a dilation of the liquefied gas to an extent that is proportional to the compressibility of the liquid. The compressibility of the liquid was taken as some function of the surface tension. They finally developed the following formula which tallied very well with experimental results:

$$V = K\left(\frac{P\sigma}{P_0}\right)^{\frac{1}{n}}$$

in which V is the volume of the condensed gas absorbed per gram of gel; i. e., the mass of the gas adsorbed divided by the density of the liquefied gas at the temperature; P is the equilibrium gas pressure; σ is the surface tension and P_0 the vapor tension of the liquefied gas at the temperature. K and $1/n$ are constants. By plotting the values of log V as ordinates and log $\frac{P\sigma}{P_0}$ — as abscissae, the experimental values of Patrick and McGavack fell on a straight line.

Since the solution of gases in liquids is also considered as a condensation, the results obtained in this investigation were also plotted according to this formula as can be noted from Fig. 10. The densities and values of the surface tension of liquid ammonia at 0° C, 20° C, and 40° C, were interpolated from the values of Berthoud[1] and the vapor tensions used were those obtained at the Bureau of Standards.[2] The results obtained for 0° C, 20° C, and 40° C, with solubilities ranging from 0.315 gram to 1.885 grams of ammonia per gram of water are so well represented by this formula, that it may be assumed that a phenomenon similar in its manifestations to that of the adsorption of sulphur dioxide by silica gel is occurring in the case of the solution of ammonia in water.

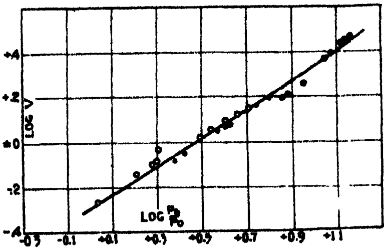

Fig. 10

Solubility of NH_3 in H_2O. ⊙ at 0° C; O at 20° C; ● at 40° C

In Curve I, Fig. 11, other available data on the solubility of ammonia in water at lower pressures obtained by Perman, Roscoe and Dittmar, and Sims, at 0° C, 20° C, and 40° C and by Mallet[3] for pressures of 743 to 744.5 mm, at −10° C, −20° C, −30° C, and −40° C, as well as the results obtained in this investigation were plotted. The results obtained in this investigation as well as by other investigators at varied temperatures and pressures, and concentrations as high as 2.746 grams ammonia per gram of water fall on the same straight line curve. This is apparently a general law for the solution of ammonia in water.

On Curve II, same figure, have been plotted in like manner the solubility of hydrogen chloride in water as found by Roscoe and Dittmar[4] at 0° C, and pressures varying from 58 to 1270

[1] Helv. Chim. Acta, I, 84–7 (1918); Jour. Chim. phys. 16, 429 (1918).

[2] Jour. Am. Chem. Soc., 42, 206 (1920).

[3] Am. Chem. Jour., 19, 804 (1897).

[4] Loc. cit.

mm. The surface tension of liquid hydrogen chloride was calculated from the work of McIntosh & Steel[1] to be 7.6 dynes; the density of liquid hydrogen chloride was taken as 0.908 according to Ansdall;[2] and vapor tension of liquid hydrogen chloride was taken as 19,900 mm according to Faraday.[3]

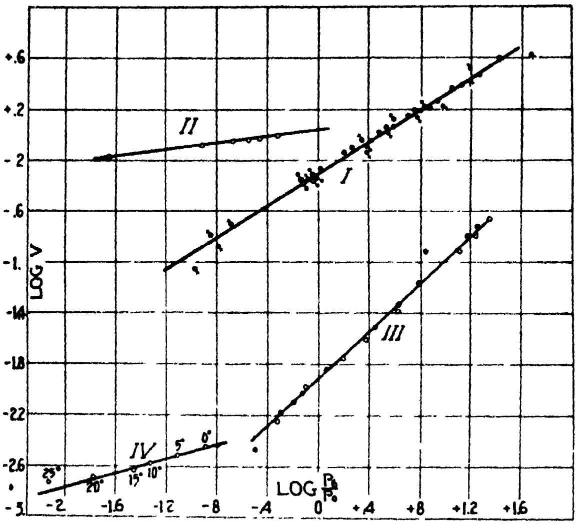

Fig. 11

On Curve I O indicates observations at 0° C; ● at 20° C; ⊖ at 40°C. † appended indicates data of Sims; ‡ data of Perman; and R data of Mallet. On Curve III O indicates data at 7° C and ● data at 20° C

On Curve III, there has been plotted the solubility of sulphur dioxide in water, as found by Sims[4] at 7° C from pressures of 27 to 1291 mm, and at 20° C, from 32.4 to 1911 mm. The values of the surface tension of liquid sulphur dioxide at 7° C and 20° C were calculated from values given by Landolt-Börnstein to be 27.2 and 24.5 dynes, respectively.

[1] Zeit. phys. Chem., **55**, 141 (1906).
[2] Proc. Roy. Soc., **30**, 117.
[3] Phil. Trans., **135**, I, 155 (1845).
[4] Loc. cit.

The density of liquid sulphur dioxide was interpolated from the data of Cailletet and Matthias[1] and taken as 1.383 for 20° C, and 1.42 for 7° C. Regnault's values for the vapor tensions were used.[2]

On Curve IV, was plotted the solubility of carbon dioxide in water at 760 mm pressure at from 0° C to 25° C. The solubility data were those of Bohr and Bock.[3] The values of surface tension at these temperatures were obtained by interpolation from data given by Landolt-Börnstein, the values used being as follows;

Temperature, C	0	5	10	15	20	25
Surface Tension	4.65	3.5	2.74	1.82	1.00	.50 dynes

The density of liquid carbon dioxide at these temperatures was obtained from the data of Warburg and v. Babo.[4] The data of Th. Tate[5] on the vapor tension of liquid carbon dioxide were used.

From the Curves I to IV it is evident that for each individual gas the law contained in the formula

$$V = K \left(\frac{P\sigma}{P_0}\right)^{\frac{1}{n}}$$

holds very well, but that these lines do not coincide. From a consideration of the nature of the solution of gases in liquids such as outlined above no such coincidence would be expected. If this formula is written in logarithmic form, there is obtained the following equation:

$$\log V = \log K + \frac{1}{n} \log \frac{P\sigma}{P_0}$$

In the above equation when $\frac{P\sigma}{P_9}P_1$ is set equal to 1, log K becomes

[1] Comptes rendus, **104**, 1565 (1887).
[2] Landolt-Börnstein Tabellen.
[3] Wied. Ann., **44**, 318 (1891).
[4] Ber. Berl. Akad., p. 509 (1882).
[5] Phil. Mag., (4), **26**, 502.

equal to log V. $1/n$ is obviously the slope of the straight line. If solutions of gases in liquids are considered as binary mixtures, it is evident that for the same solvent, those gases which in the liquefied state mix in all proportions with water (an indication that their molecular forms are such that the molecules of the one liquid fit into the pores of the other liquid) their condensates will be taken up in greater quantity than those of gases whose condensates have only a limited miscibility with water. Besides the degree of miscibility, such factors as the dielectric constant of the liquefied gas (which is a function of the space occupied by the molecules), no doubt play an important rôle in determining the degree of solubility. It is proposed that the values of the constants K and $1/n$ depend on such factors as miscibility and dielectric constants of the liquefied gases, etc. In fact from a comparison with Fig. 11 it becomes evident that K is much greater for the solubility curves of ammonia and hydrogen chloride, which in the liquid state are miscible with water in all proportions than for carbon dioxide or sulphur dioxide whose condensates have only a limited solubility in water. Also, in the case of these four gases, it has been found that the values of $1/n$ parallel to some extent the values of the dielectric constant of the liquefied gas dissolved, i. e., those gases whose liquids possess a high dielectric constant have a large value of $1/n$. But unfortunately, there are not enough data available for other gases to test out the validity of this relation.

However, this fact is worthy of note—that the values of K and $1/n$ for each particular gas are independent of the temperature and the partial pressure of the dissolved gas. This fact is of great importance; and, though only speculation as to its significance is possible at present, it offers very fertile fields for investigation as to the factors on which the values of these constants depend in the application of the adsorption formula to the case of the solubility of gases in liquids.

Summary

(1) A static method has been developed for measuring

the partial pressure of a component which is relatively very small compared to the partial pressure of the second component.

(2) This method has been used to determine the partial pressures of water and ammonia of concentrated ammonia solutions at 0° C, 20° C, and 40° C, at partial pressures of ammonia varying from 1000 to 4000 mm. The partial pressures of the ammonia were measured to within 4 to 2 millimetres; and those of the water to 0.08 millimetre.

(3) The solubility of ammonia in water was determined at 0° C, 20° C, and 40° C at pressures from 750 to 3600 mm. The densities of these solutions were also determined.

(4) A theory of the nature of solutions of gases in liquids first advanced by Graham, has been amplified, and solutions of various gases in liquids classified on the basis of some of the physical and chemical properties of the gas.

(5) The formula

$$V = K\left(\frac{P\sigma}{P_0}\right)^{\frac{1}{n}}$$

has been found to represent well the solubility of ammonia hydrogen chloride, sulphur dioxide, and carbon dioxide in water at varied temperatures and pressures. In this formula V is the volume occupied by the liquefied gas dissolved per gram of water; P_0 is the vapor tension and σ the surface tension of the liquefied gas at the temperature while P is the equilibrium gas pressure. The constant K for ammonia has the value 0.49 and $1/n$ has the value 0.69.

(6) Solubility data of HCl, SO_2, and CO_2 have also been plotted according to this formula.

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THE NATURE OF SECONDARY VALENCE. PART IV

BY HOMER W. SMITH

Partition Coefficients in the System Glycerine : Acetone

§ 1. Introduction

In the experimental work thus far presented, water has always been used as one of the solvents. Since water is unique in its physical properties, it seemed possible that the results obtained in these systems might be modified to a great extent in systems composed of non-aqueous liquids. For this reason, a large amount of work has been done in the system glycerine : acetone. Glycerine takes the part of water and acetone the part of the organic solvent.

In preliminary experiments, a commercial grade of glycerine was heated in a distilling flask at 140° C for two hours. This sample on trial gave the same results as did the original material and consequently the original was used with out preliminary heating.[1] It furthermore checked in a satisfactory manner other lots from the same and other sources so that it is improbable that any systematic error entered from this direction.

The acetone was carefully redistilled from a mixture of equal parts of calcium oxide and calcium chloride. Since the acid-acetone was repeatedly recovered in this manner, it is certain that the product was anhydrous and free from serious contaminations.

The acid phthalate salts were made by mixing standardized solutions of phthalic acid on the one hand, and the desired amine on the other, in the proportions of two to one. It was assumed that the remaining titratable hydrogen of the phthalic acid represented one molecule of the amine acid-salt.

It was necessary to design a special container for this study, since the glycerine cannot be measured from one

[1] Eastman Research Lab. Practical.

flask to another with any accuracy. A number of glass, pistol-shaped flasks were devised. Each consisted of a bulb of definite volume (corresponding to the pistol grip) opening at an angle of 75° into a tube of larger volume (corresponding to the pistol barrel). The neck between the bulb and cylinder was made small, and so graduated that each bulb held exactly the same volume of liquid (33.2 cc ± .05 cc). The glycerine was run directly from a gravity bottle into the bulb by means of a suitable delivery tube, thus facilitating the accurate delivery of a given volume of glycerine. An *equal volume* of the acetone solution of known titer was then added, the cylinder mouth stoppered and shaken for a few moments to secure an initial mixing. The mixture was then brought to the desired temperature and shaken for two or three minutes. (It is

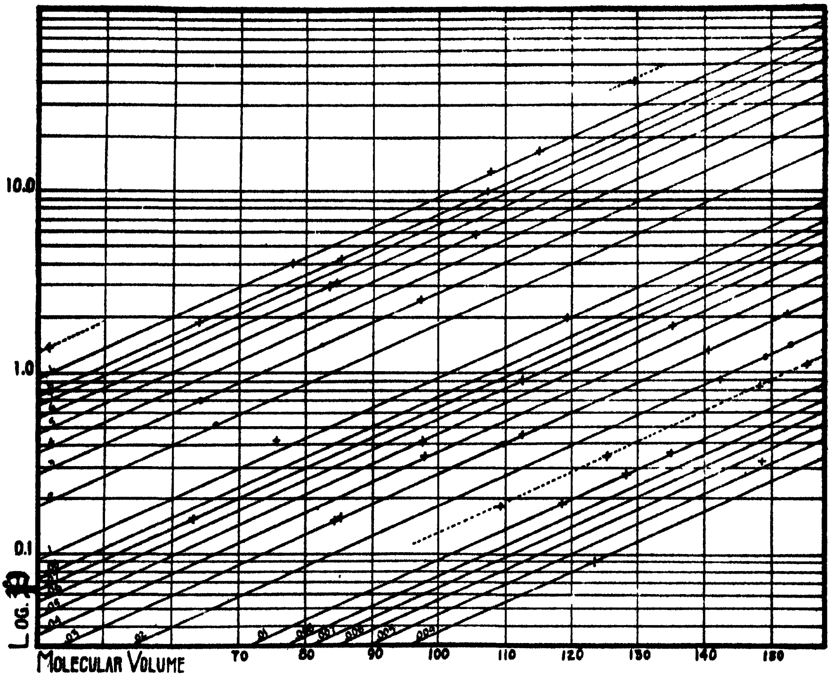

Fig. 1
The Partition Coefficients ($C_2 = 1\ m/L$) in the System Acetone: Glycerine

probable that a half-minute's shaking brings the mixture to equilibrium.) After shaking, the acetone, being the liquid of lesser density, can be drawn directly into a pipette inserted through the cylinder mouth. All solutions were made in acetone and titrated with standard aqueous acid or alkali. The concentration in the glycerine was determined by difference.

§ 2. General Considerations

The general picture is the same as it was in the previous systems. It is therefore not necessary to describe it in detail. This system puts the method of correction to a much more severe test, however, because after shaking equal volumes of acetone and glycerine together, the acetone layer loses about 17% in volume, the glycerine increasing 15%, and the total volume decreasing 2%. Thus we are not determining the partition coefficient of the solute between pure acetone and pure glycerine, but between two mixtures of acetone and glycerine. Since the concentration in the glycerine is determined by difference, and on a volume basis, it might be expected that the change in volume which occurs when the two liquids are mixed would introduce a serious complication. The decrease in volume of the acetone layer would necessitate an increase in concentration of the solute, were the solute unable to pass into the glycerine layer. We will see that this actually does take place in some instances. But, where partition does take place, if we deal with concentrations per unit volume of solvent, the facts show that the relative results are not modified. It is probable, however, that the absolute value of the series constants are modified, but this point will not be treated in detail until we consider the relations between the series constants in various systems.

One of the most important points brought out by the data in Table I is the fact that the *absolute values* of the *series constants for the amines and the acids are identical in the system glycerine : acetone.* Consequently the amine and the acids have been considered together in the following tables.

TABLE I

Partition Coefficients of the Amines and Acids in the System Glycerine : Acetone

Series number	a	V_m	C_2	$\mathfrak{P}$ obs.	$\mathfrak{P}$ calc.
Benzilic acid Benzoic acid α-β-Dinitropropionic acid 2.4-Dinitrobenzoic acid Salicylic acid 2.4.6-Trinitrobenzoic acid *n*-Valeric acid		These compounds pass completely into the acetone layer.			
1.414	+1.45154				
Formic acid		41.5	1	1.36	1.39
α-Bromopropionic acid		105.8	10	16.2	16.4
iso-Valeric acid		129.5	1	40.0	40.7
1.0	+1.30103				
Chloroacetic acid		78.0	1	3.90	3.99
n-Butyric acid		107.8	1	12.70	12.52
.8	+1.20412				
Acetic acid		64.0	1	1.85	1.86
Thiacetic acid		73.6	10	2.65	2.69
Propionic acid		85.3	1	4.20	4.22
Dichloroacetic acid		97.2	10	7.0	6.67
Sec-Butyric acid		107.3	1	9.68	9.83
.7	+1.14613				
Propionic acid		85.3	10	3.55	3.69
.6	+1.07918				
Bromoacetic acid		84.5	1	3.13	3.58
.5	+1.00000				
Ethyl amine		64.6	10	1.20	1.20
α-Bromopropionic acid		105.8	1	5.80	5.80
.4	+0.90309				
Thiacetic acid		73.6	1	1.45	1.35
.3	+0.77815				
Ethyl amine		64.6	1	0.71	0.716
Dimethyl amine		66.3	10	0.67?	0.764
Dichloroacetic acid		97.2	1	2.50	2.50
.2	+0.60206				
Dimethyl amine		66.3	1	0.50	0.502
.1414	+0.45154				
Trichloroacetic acid		119.5	10	2.65	2.77
.1	+0.30103				
Trichloroacetic acid		119.5	1	1.95	1.96
.08	+0.20412				

Series number	a	V_m	C_2	Λ obs.	Λ calc.
Anthranilic acid		135.0	10	2.92	2.84
.07	+0.14613				
Fumaric acid		112.6	10	1.02	1.05
Triethyl amine		152.6	10	4.9	4.89
.06	+0.07918				
Diethyl amine		109.3	10	0.81	0.795
Fumaric acid		112.6	1	0.89	0.888
Dipropyl amine		151.5	10	3.75?	4.02
.05	±0.00000				
Malonic acid		97.8	1	0.443	0.427
Anthranilic acid		135.0	1	1.80	1.78
.04	—0.09691				
.03	—0.22185				
Diethyl amine		109.3	1	0.42	0.398
Maleic acid		112.6	1	0.457	0.452
Succinic acid		120.0	1	0.603	0.600
n-Methylpiperidine		133.8	10	0.99	1.02
Bromosuccinic acid		140.5	1	1.25	1.38
Mandelic acid		152.2	1	2.05	2.06
.02	—0.39794				
Piperidine		108.8	1	0.275	2.60
Dipropyl amine		151.5	1	1.20	1.34
Triethyl amine		152.6	1	1.40	1.40
.01414	—0.54846				
o-Phthalic acid		155.6	1	1.09	1.11
.01	—0.69897				
Malic acid		118.8	1	0.192	0.191
Gallic acid		135.0	1	0.352	0.356
.008	—0.79588				
.007	—0.85387				
.006	—0.92082				
Hippuric acid		178.7	1	1.16	1.14
.005	—1.00000				
.004	—1.09691				
Tartaric acid		123.6	1	0 090	0.0918
.0001414	—2.54846				
Dimethyl amine-acid-phthalate		220.1	1	0.128	0.132
.00007	—3.85387				
Trimethyl amine-acid-phthalate		243.6	1	0.157	0.161
.00003	—3.22185				
Piperidine-acid-phthalate		264.4	1	0.155	0.153
Diethyl amine-acid-phthalate		264.9	1	0.158	0.156
.00001414	—3.54846				
n-Methylpiperidine-acid-phthalate		289.4	1	0.180	0.188
Dipropyl amine-acid-phthalate		305.5	1	0.335	0.349
.00001	—3.69897				

TABLE I (*Continued*)

Series number	*a*	V_m	C_2	P obs.	P calc.
Trimethyl amine-acid-phthalate		308.2	1	0.270	0.274
.000005	—4.00000				
Benzylethyl amine-acid-phthalate		328.6	1	0.313	0.299
Di-*iso*butyl amine-acid-phthalate		346.7	1	0.60	0.600
.000003	—4.22185				
Tripropyl amine-acid-phthalate		378.1	1	1.18	1.21
.000001414	—4.54846				
Di-*iso*amyl amine-acid-phthalate		388.1	1	0.816	0.831

	V_m	C_2	P obs.	*a* calc.	Corresponding series
Chloroacetic acid	78.0	10	4.45	+1.34836	1.115
Piperidine	108.8	10	0.45	—0.16012	.03458
n-Methylpiperidine	133.8	1	0.57	—0.47413	.01678
Glutaric acid	142.2	1	0.88	—0.42750	.01877
o-Phthalic acid	155.6	10	1.28	—0.48612	.01633
Gallic acid	135.0	1	0.352	—0.74757	.008942

§ 3. The Series Behavior

It was shown in the previous communication that a series must be recognized between Series 1 and Series 2; a value of 1.414 was arbitrarily assigned to this series, and it has been included in the above table. Compounds not falling in the recognized series are given at the end of the table. Note that *n*-methylpiperidine, glutaric acid and phthalic acid give an average value of .01729 which approximates a series corresponding to the $\sqrt{3}$, or 1.732.

Reference to the following experimental section will show that in many cases the ratio C_A/C_G is constant. For the rest, this ratio increases in about as many cases as it decreases. It is not known whether association in one solvent or dissociation in the other is the predominant factor; but whatever the cause of the inconstant ratio, the interpolation method of obtaining the partition coefficient yields results which are in excellent agreement with those compounds which show a constant distribution ratio, so far as the series behavior is concerned.

The number of compounds occurring in the various series is as follows:

Series			$C_2 = 1\ m/L$	$C_2 = 10\ m/L$
1.414,	.1414,	etc.	6	2
1.0	.1	etc.	6	0
.8	.08	etc.	3	3
.7	.07	etc.	1	2
.6	.06	etc.	3	2
.5	.05	etc.	6	1
.4	.04	etc.	2	0
.3	.03	etc.	10	2
.2	.02	etc.	4	0

Another important point is that some compounds pass completely into the acetone layer. On the supposition that the fundamental forces involved in this behavior are discontinuous in nature, both as regards the solute and the solvents, it is not surprising that limiting conditions could exist whereby a solute would pass completely in just this way, into one or the other solvent. That is, in a mechanism working by abrupt changes, there must both be a maximum and a minimum activity, and in any system in which one of these limits was reached, the all (unit) or none principal would necessitate complete concentration of the solute in one solvent or the other. Evidence in this direction was seen in the system water: xylene, where it was found that xylene did not extract perceptible amounts of the dibasic acids and other compounds It was thought at that time that this was largely a matter of experimental error, for the predicted partition coefficients were so low that they were difficultly determined. But when the reverse situation is found in this system, i. e., when the solute passes entirely into the organic solvent, it seemed probable that this failure to get a perceptible distribution is a real and not an apparent failure of the distribution law. In general we know that with increasing length in the carbon chain, there comes a time when the solubility in water falls off abruptly; this fact is rendered more intelligible by the recognition of the existence of *abrupt, limiting conditions* in intermolecular relations.

As an example consider the simple aliphatic acids; acetic, propionic, and *sec*-butyric occurring in Series 8, *n*-butyric in Series 1.0 and *iso*-valeric in Series 1.414. One is led to look for *n*-valeric in Series 2, where it would have a partition coefficient of about 59.0, a determinable value. Contrarily, in this and other similar instances the concentration of the solute in the acetone layer is increased (per unit volume) by the diminution in volume of this layer. This increased concentration makes the failure of the distribution law even more apparent.

§ 4. The Acid-Phthalate Salts

The original intention in including some salts of this nature in this study was to determine whether the series constants for the salts would be in agreement with the acids or the amines, or different from both of these. It has been found, however, that the acids and the amines have identical series constants so that this question remains unsettled. It cannot be satisfactorily settled by studying any of the systems previously used containing water, because the partition coefficients in these systems are too small to be determinable with any accuracy. Though little significance can be attached to the fact that the salts do have the same series constants as the amines and acids, it is a very satisfactory way to have the thing work out.

Summary

1. The partition coefficients of fifty acids, amines, and acid-phthalate salts have been determined in the system glycerine : acetone. The results yielded by these data are in excellent agreement with the results obtained in the systems previously studied.[1]

2. A fact not brought out by previous studies is that under certain conditions concerning the nature of the solvents and solute, a solute is not distributed, but is concentrated entirely in one or the other of the solvents.

[1] Jour. Phys. Chem., **25**, 160, 204, 605 (1921).

3. It is a noteworthy point that the series constants for the acids and the amines (and the amine salts of phthalic acid) have the same absolute value in this system, as contrasted with the different values found in systems containing water as one solvent.

Experimental. Section IV

The Partition Coefficients of the Amines, Acids and Acid-Phthalate Salts between Glycerine and Acetone, 25°

The following compounds pass completely into the acetone layer:

- Benzilic acid
- Benzoic acid
- α-β-Dibromopropionic acid
- 2.4-Dinitrobenzoic acid
- Di-*iso*butyl amine
- Salicylic acid
- 2.4.6-Trinitrobenzoic acid
- *n*-Valeric acid

	C_G	C_A	C_A/C_G	[illegible]
Acetic acid	17.30	29.30	1.69	
	10.00	17.60	1.76	
	4.85	8.60	1.77	
	4.60	8.20	1.78	
	3.875	7.00	1.81	
	2.775	4.775	1.72	
	2.77	4.70	1.70	
	1.6	3.025	1.80	
	1.00	1.825	1.82	*I*
	0.9425	1.725	1.83	1.85
Anthranilic acid	4.60	14.70	3.20	*IO*
	3.20	8.95	2.80	2.92
	1.55	3.80	2.45	*I*
	1.05	2.20	2.09	1.80
Benzylethyl amine-acid-phthalate	10.35	3.65	0.302	
	7.80	2.55	0.327	
	5.45	1.80	0.330	

TABLE (*Continued*)

	C_G	C_A	C_A/C_G	[illegible]
	3.975	1.30	0.327	Mean
	2.525	0.70	0.277	0.313
Bromoacetic acid	4.35	14.20	3.26	
	2.25	7.25	3.22	
	1.60	4.70	2.94	Mean
	0.645	2.00	3.10	3.13
α-Bromopropionic acid	0.90	20.65	23.0	*10*
	0.70	11.20	16.0	16.2
	0.4875	6.7625	13.9	
	0.40	4.50	11.2	
	0.30	2.62	8.73	*1*
	0.21	1.42	6.75	5.80
Bromosuccinic acid	7.675	11.575	1.51	
	3.925	5.575	1.42	
	1.775	2.375	1.34	*1*
	1.28125	1.625	1.27	1.25
n-Butyric acid	2.10	26.65	12.7	
	1.15	14.60	12.7	
	0.50	6.4375	12.8	Mean
	0.275	3.45	12.5	12.7
sec-Butyric acid	2.20	20.20	9.2	
	1.30	11.85	9.14	
	0.65	6.80	10.45	
	0.625	6.825	9.90	
	0.375	3.375	9.00	Mean
	0.350	3.40	9.72	9.68
Chloroacetic acid	6.15	29.25	4.76	*10*
	3.125	15.925	4.60	4.45
	2.00	8.60	4.30	
	0.975	3.90	4.00	*1*
	0.325	1.30	4.00	3.90
Dichloroacetic acid	2.40	37.9	15.8	*10*
	1.90	17.8	19.38	7.0
	1.375	9.725	7.07	
	0.925	4.625	5.02	
	0.61	2.20	3.61	*1*
	0.43	0.83	1.93	2.5
Diethyl amine	18.10	15.80	0.873	*10*
	6.55	4.50	0.687	0.81
	6.775	4.70	0.693	
	3.375	1.75	0.518	*1*
	1.75	0.625	0.357	0.42

	C_G	C_A	C_A/C_G	D
Diethyl amine-acid-phthalate	12.80	1.65	0.129	
	9.975	1.325	0.133	
	6.65	1.05	0.158	
	4.15	0.775	0.187	*1*
	2.0375	0.450	0.221	0.158
Di-*iso*-amyl amine-acid-phthalate	7.85	6.15	0.783	
	6.30	4.80	0.762	
	4.875	3.625	0.744	
	3.075	2.725	0.886	Mean
	1.9375	1.750	0.905	0.816
Di-*iso*-butyl amine-acid-phthalate	9.65	4.45	0.462	
	7.60	3.80	0.500	
	5.85	3.10	0.530	
	3.95	2.10	0.530	*1*
	1.90	1.10	0.580	0.60
Dimethyl amine (anhydrous)	27.8	20.1	0.723	*10*
	15.8	10.6	0.672	0.67
	7.525	4.775	0.635	
	4.325	2.425	0.561	*1*
	2.25	1.125	0.510	0.50
Dimethyl amine-acid-phthalate	14.75	1.70	0.115	
	10.875	1.30	0.119	
	7.80	1.00	0.128	
	5.4875	0.8125	0.148	*1*
	3.725	0.6250	0.168	0.128
Dipropyl amine	2.75	10.1	3.67	*10*
	2.275	8.775	3.64	3.75
	2.025	5.425	2.69	
	1.60	3.85	2.40	
	1.50	2.90	1.93	
	1.325	1.925	1.45	*1*
	0.925	1.30	1.40	1.2
Dipropyl amine-acid-phthalate	10.90	2.45	0.224	
	7.625	1.825	0.239	
	4.525	1.35	0.298	
	2.50	0.8875	0.335	*1*
	1.45	0.600	0.413	0.335
Ethyl amine	8.20	9.76	1.19	*10*
	4.72	4.76	1.01	1.20
	4.55	4.65	1.02	
	2.70	2.25	0.835	
	1.76	1.26	0.715	
	1.625	1.25	0.77	*1*
	1.20	0.67	0.558	0.71

TABLE (*Continued*)

	C_G	C_A	C_A/C_G	[illegible]
Formic acid	16.0	20.8	1.30	
	5.65	7.8	1.38	
	3.70	5.65	1.39	
	2.0625	2.8875	1.40	Mean
	1.525	2.075	1.36	1.36
Fumaric acid	5.275	5.175	0.981	*10*
	2.225	2.125	0.954	1.02
	1.3375	1.1875	0.888	*1*
	0.730	0.6350	0.870	0.89
Galic acid	29.85	9.55	0.320	*10*
	12.85	4.45	0.346	0.318
	6.625	2.325	0.351	*1*
	2.45	0.8625	0.352	0.352
Glutaric acid	9.65	8.15	0.845	
	3.025	2.60	0.860	
	2.950	2.575	0.874	
	1.55	1.350	0.870	*1*
	0.875	0.775	0.885	0.880
Hippuric acid	19.85	22.80	1.15	
	8.20	9.70	1.18	
	4.10	4.80	1.17	Mean
	12.40	2.75	1.15	1.16
Maleic acid	3.05	6.85	0.525	
	7.40	3.50	0.473	
	32.85	1.75	0.454	
	1.50	0.95	0.380	Mean
	1.925	0.4375	0.454	0.457
Malic acid	11.0625	2.2875	0.207	
	5.50	1.10	0.200	
	3.75	0.675	0.180	*1*
	2.60	0.475	0.182	0.192
Malonic acid	14.0	6.05	0.433	
	6.05	2.80	0.462	
	3.775	1.8875	0.500	
	2.4875	1.05	0.423	Mean
	1.20	0.475	0.396	0.443
Mandelic acid	11.6	23.0	1.98	
	8.25	16.45	1.99	
	4.25	8.65	2.04	*1*
	2.075	4.225	2.04	2.05
n-Methylpiperidine	20.8	22.2	1.068	*10*
	11.05	11.15	1.010	0.99

	C_G	C_A	C_A/C_G	[illegible]
	6.40	6.10	0.954	
	3.50	3.10	0.886	
	2.68	2.06	0.767	
	2.00	1.375	0.687	
	1.73	0.95	0.550	
	1.30	0.65	0.500	1
	1.03	0.29	0.282	0.57
n-Methylpiperidine-acid-phthalate	12.75	1.76	0.138	
	4.55	0.90	0.198	
	2.460	0.680	0.276	1
	1.280	0.480	0.375	0.180
o-Phthalic acid	6 375	8.025	1.26	10
	3.200	3.800	1.19	1.28
	1.5875	1.775	1 12	1
	0.8750	0.9375	1.07	1.09
Piperidine	33.3	16.0	0.48	10
	23.4	10.6	0.453	0.45
	17.35	7.8	0.45	
	12 00	4.925	0.41	
	9.95	4.0	0.402	
	6.775	2.375	0.350	
	5.45	1.875	0.344	
	3.25	0.85	0.262	
	2.85	0.725	0.254	1
	1.3125	0.225	0.144	0.275
Piperidine-acid-phthalate	10.31	1.475	0.143	
	3.86	0.700	0.181	
	1.85	0.482	0.261	
	0.79	0.369	0.467	1
	0.356	0.250	0.702	0.155
Propionic acid	9.60	31.00	3.23	10
	5.80	19.40	3.34	3.55
	3.50	10.85	3.10	
	2.15	7.45	3.46	
	1.48	5.76	3.89	
	0.78	3.06	3.93	1
	0.43	1.74	4.05	4.20
Succinic acid	5.70	3.275	0.575	
	4.725	2.925	0.619	
	2.675	1.550	0.580	
	1.9625	1.325	0.675	Mean
	1.35	0.7625	0.565	0.603?
Tartaric acid	16.25	1.30	0.080	
	16.25	1.25	0.077	

TABLE (*Continued*)

	C_G	C_A	C_A/C_G	P
	6.00	0.60	0.100	
	5.77	0.625	0.105	
	3.075	0.425	0.136	
	2.75	0.4125	0.150	*1*
Thiacetic acid	9.40	30.10	3.20	0.090
	4.60	14.30	3.10	*10*
	3.60	9.40	2.62	2.65
	2.36	5.36	2.27	
	1.56	3.04	1.95	*1*
Trichloroacetic acid	1.70	20.90	12.30	1.45
	1.25	7.70	6.17	*10*
	1.075	5.40	5.02	7.55
	0.7625	2.8375	3.72	
	0.600	1.50	2.50	*1*
Triethyl amine	3.20	25.80	8.06	1.95
	2.25	13.20	5.87	*10*
	1.65	6.35	3.85	4.9
	1.175	2.875	2.44	
	0.865	1.470	1.70	*1*
Triethyl amine-acid-phthalate	12.775	2.70	0.2115	1.40
	9.35	2.00	0.214	
	5.60	1.45	0.259	
	4.075	1.10	0.270	*1*
	2.35	0.70	0.398	0.270
Trimethyl amine-acid-phthalate	13.55	1.95	0.144	
	10.35	1.50	0.145	
	5.65	0.90	0.159	*1*
	4.20	0.70	0.167	0.157
Tripropyl amine-acid-phthalate	6.80	4.25	0.625	
	4.45	3.125	0.702	
	2.55	2.125	0.843	*1*
	1.375	1.400	1.020	1.18
iso-Valeric acid	0.500	23.00	46.0	
	0.300	10.30	34.4	
	0.1375	5.15	37.4	Mean
	0.1125	4.75	42.3	40.0

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PURE ANILINE AND WATER EMULSIONS

BY SHANTI SWARUPA BHATNAGAR

Effects of the Distance of Globules on the Rate of Coagulation by Electrolytes

The work of McC. Lewis,[1] Ellis[2] and Powis has established that a neutral oil emulsion behaves like a model suspension colloid, and that its stability is largely dependent on the charge on its particles as is also the case with many suspensoids.

The influence of electrolytes on the rate of coagulation of emulsions has also been studied by Hatschek.[3] He used emulsions in which the disperse phase was of the same specific gravity as the continuous medium. In this case, when electrolytes were added, coalescence of the particles took place whenever the Brownian movement brought the globules into contact. As the effect of gravity was eliminated the increase in size ceased when the Brownian movement became too slight to bring the globules into contact.

In preparing these emulsions Hatschek used alcohol or acetone in order to make the two phases of equal density. The introduction into the system of a foreign substance like acetone or alcohol may introduce complications. Such complications have been, in fact, noticed by investigators on suspensoids.[4]

In order to minimize the errors which may arise on account of these complications, the author chose pure aniline and water emulsions for examination. If aniline and water are put together in a beaker at room temperatrue (17°–18°), aniline being heavier than distilled water at that temperature it lies at the bottom of the beaker, and the water forms a layer above it. If the beaker be now slowly warmed, it is observed that at about 46°–47° when the densities of the two

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[1] Koll. Zeit., 5, 91 (1909).
[2] Trans. Faraday Soc., 9, 14 (1913).
[3] Koll. Zeit., 9, 159 (1911).
[4] Zsigmondy: Kolloidchemie (1921).

phases, partly due to the solubility of aniline in water and partly because of the temperature, approach equality, the slightest stirring produces a fine milky emulsion. If the two are now shaken vigorously even for ten minutes, a fairly stable emulsion is obtained. If preserved in a clean flask at that temperature, the emulsion remains stable for days and does not seem to show any signs of separation. This is more especially so if the amount of aniline in suspension is smaller than 1 in 1000 parts of water.

Aniline emulsions have been shown to be exceptionally fine-grained[1] and are quickly coagulated by electrolytes and are therefore specially suited for such investigations.

Experimental

The emulsions were prepared by heating 80 cc of pure aniline with 1000 cc of water to about 80° in a flask with a constricted neck in order to prevent the condensation of the drops of the liquid. A dense emulsion was formed. The flask was then corked and shaken for about ten minutes by hand and for about the same time in a powerful mechanical shaker. It was then transferred to a thermostat regulated at 46° C at which temperature, the preliminary trials showed the emulsions to be fairly stable. The emulsion was kept there for several hours when it separated into two layers. The two layers were separated by means of a separating funnel and the thin emulsion which lay at the bottom of the flask was transferred to a carefully cleansed resistance glass flask and kept stoppered.

The amount of aniline present in the emulsion was estimated by the colorimetric method of E. Elgrove.[2] The test is based on the colouration given to an aniline solution when reacted on by calcium hypochlorite. The colour is compared with standard aniline solutions in Nessler jars and by this means as little as 0.01 mg of aniline in 20 cc may be readily detected.

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[1] McC. Lewis: Loc. cit.

[2] Jour. Ind. Eng. Chem., 9, 953 (1917).

It may be noted that by this method the total concentration of aniline in the emulsion is estimated, but all of it is not present in the form of globules, as aniline is soluble in water. Let the total amount of aniline in v volume of the emulsion be represented by x, and let x' be the amount dissolved, then $x-x'$ represents the amount of aniline in suspension and $x-x'/v$ the concentration of globules per unit volume.

The result obtained by analysis gave the total amount of aniline in a litre of emulsion equal to 43.541 g. The solubility of aniline in water at 46° is given by 41.0, so that the amount of aniline present in the form of globules was 2.54 g per litre. The emulsions were diluted thrice by water saturated with aniline at 46°, and the amount of suspended aniline was 0.847 g per litre.

The procedure adopted in examining the rate of coagulation was to note the amount of time required to produce a perceptible change corresponding to a certain definite degree of turbidity, when a definite amount of electrolyte was added. 5 cc of emulsion diluted with 5 cc of water saturated with aniline was kept in a separate test-tube as a standard for convenience of comparison.

5 cc of electrolyte and 5 cc of emulsion in two separate test-tubes were immersed in a beaker containing water which was suspended inside a thermostat. About one-fifth of the length of the tubes remained above the surface of water. In order to minimize the errors in measuring the volumes, the same two pipettes were always used, one for the emulsion and the other for the electrolytes in order to keep the relative volumes constant. After the liquids in the tube had acquired the temperature of the bath, they were withdrawn and the electrolyte was added to the emulsion. This test-tube was then again immersed in the beaker. The process of pouring the electrolyte into the emulsion did not take more than 25 to 30 seconds. The test-tube was taken up from time to time and observed. Several concentrations of the electrolytes and emulsions were examined. The emulsions were always diluted

by water saturated with aniline at that temperature. The electrolytes studied were potassium chloride, sodium sulphate and chloride, barium chloride, strontium chloride, chromium sulphate and aluminium sulphate.

The results are shown in Tables I–III.

TABLE I

Electrolyte	Concentration g equivalent per litre	Times required for first perceptible change
Potassium chloride	0.05	5 hours
	0.08	2 hours 5 minutes
	0.10	41 minutes
	0.139	In about 12 mins. 8 sec.
Sodium chloride	0.05	Not for 5 hours
	0.10	43 minutes
	0.142	In about 12 minutes
Sodium sulphate	0.10	Not for 5 hours
	0.21	29 minutes
	0.28	In about 13 minutes

TABLE II

Electrolyte	Concentration g equivalent per litre	Times required for first perceptible change
Barium chloride	0.018	1 hour 30 minutes
	0.020	1 hour
	0.029	10 minutes
	0.040	2 minutes
Strontium chloride	0.02	1 hour 15 minutes
	0.026	1 hour
	0.032	8 minutes

TABLE III

Electrolyte	Concentration g equivalent per litre	Times required for first perceptible change
Chromium sulphate	0.001	1 hour 15 minutes
	0.002	13 minutes
	0.005	About 4 minutes
Aluminium sulphate	0.001	1 hour
	0.002	10 minutes 2 seconds
	0.005	About 2 minutes

Effect of Dilution on the Rate of Coagulation

There is at present very little quantitative data on the effect of dilution on the rate of coagulation of suspensoids. The work of Woodstrau, Zsigmondy, Westgren and Reitstötter[1] and Mukherjee[2] shows that the dilution makes the suspensoids more stable as far as the effects of electrolytes are concerned. The increasing stability of pure oil and water emulsions with the decreasing amount of the dispersed phase has been observed by Wa. Ostwald, Lewis, Ellis, and Hatschek.[3] The effect of dilution on the rate of coagulation of emulsions by electrolytes has not been studied. The following experiments were performed to investigate this effect and to see how far the behaviour of emulsions in this respect agrees with that of various suspension colloids.

In investigating these effects the same procedure has been followed as described above and the emulsions have always been diluted by the addition of water saturated with aniline at 46° C. If this precaution is not taken and pure water is added for dilution, some of the aniline globules will go into

TABLE IV

Electrolyte		Time for perceptible change for standard emulsion	For twice diluted	For thrice diluted	For four times diluted
Potassium chloride	1	41 mins.	56 mins. 1 sec.	115 mins. 5 sec.	133 mins. 10 sec.
	2	12 mins. 8 sec.	20 mins. 5 sec.	41 mins.	63 mins. 9 sec.
Barium chloride	1	2 mins.	4 mins. 6 sec.	7 mins.	13 mins. 2 sec.
	2	10 mins.	18 mins. 7 sec.	27 mins. 5 sec.	40 mins.
Aluminium sulphate	1	10 mins.	11 mins. 1 sec.	13 mins. 5 sec.	15 mins. 9 sec.
	2	2 mins.	2 mins. 53 sec.	3 mins. 58 sec.	7 mins. 2 sec.

[1] Zeit. phys. Chem., **92,** 750 (1918).
[2] Jour. Chem. Soc., **117,** 1569 (1920).
[3] Loc. cit., **117,** 1569 (1920).

solution and comparable results will be impossible. Some of the results obtained are shown in Table IV.

At the request of Zsigmondy who studied the process of the coagulation of gold sols., under the ultramicroscope in various dilutions, Smoluchowski developed a mathematical hypothesis of the kinetics of coagulation[1] and deduced the equation:

$$\frac{1}{T} = 4\pi D\, Rn_0 = \frac{1}{t}\left\{\sqrt{\frac{n_0}{n}} - 1\right\}$$

when t is the time in seconds, D is the diffusion constant, R the radius of particles, n_0 the number of primary particles. From this equation it is evident that coagulation time T of a given solution can be lengthened as desired by dilution, even when considering the case of instantaneous coagulation, for T is directly proportional to n_0.

The equation is more simply represented as

$$n_t = \frac{n}{1 + \frac{t}{T}}$$

where n is the total number of particles in unit volume just after mixing the sol with electrolyte (time zero), n_t is the number at time t in seconds and T is the characteristic of the rate of coagulation.

The absolute quantitative verification of this equation is not possible. Since in general the rate of coagulation is defined by the time taken to produce a definite change in the turbidity of the emulsion, the standard of comparison of one emulsion is arbitrary to the other. The manner in which any of the properties of the emulsion change with the progress of coalescence is very complicated and no relationship between these physical properties and the average size of the aggregate is known. These indirect methods, therefore, lose a quantitative basis for comparison. At the same time there can be no

[1] Zeit. phys. Chem., 92, 192 (1917).

doubt as to the qualitative nature of the effect observed and the results are evident from Table IV.

The effects of electrolytes in general are the same as in the case of many sols, the trivalent electrolytes being more effective than the bivalent ones and the bivalent more than the univalent ones.

The order of the precipitating efficiency of the electrolytes is given by

$$Al > Cr > Ba > Sr > K > Na$$

It is interesting to note that this order has been observed on many suspensoid systems; thus for

(1) Gold.[1] Al > Ba > Sr > Ca > Hg > H > Cs > Rb > K > Na > Li

(2) Platinum.[2] Al, Ph > Ba > K > Na

(3) Copper Ferrocyanide.[3] Al > Ba > H > CS > Rb > K > Na > Li

(4) Prussian Blue.[4] Al > Ba > H > CS > Rb > K > Na > Li

(5) Silver.[5] Al > Ba, Sr, Ca > H > CS > Rb > K > Na > Li.

Thus the analogy between aniline and neutral oil emulsions of McC. Lewis and Ellis, and various suspensoids is completely established.

[1] Galecki: Zeit. anorg. Chem., **74**, 174 (1912); Westgren: Arkiv. Kem. Min. Geol., **7**, No. 6, 1–30 (1918). "Chemistry of Colloids," by Taylor.

[2] Freundlich: Kapillarchemie, 352 (1909).

[3,4] Pappadà: Koll. Zeit., **6**, 83 (1910); **9**, 136 (1911).

[5] Pappadà: Gazz. chim., **42**, I, 263 (1912).

THE INFLUENCE OF THE CONCENTRATION OF COLLOIDS ON THEIR PRECIPITATION BY ELECTROLYTES

BY HARRY B. WEISER AND HENRY O. NICHOLAS

The influence of the concentration of colloids on their precipitation by electrolytes has been studied by a number of investigators. The first work of this kind was done by Freundlich[1] using colloidal arsenious sulphides. The results of his investigations are given in Table I.

TABLE I

Electrolyte	Concentration of colloid, millimoles per 1	Precipitation value, millimoles per 1	$\frac{a}{b}$
$BaCl_2$	19.15	(a) 1.050	1.09
$BaCl_2$	14.71	(b) 0.964	
$Ca(NO_3)_2$	19.15	(a) 0.955	1.01
$Ca(NO_3)_2$	14.71	(b) 0.945	
$BaCl_2$	15.41	(a) 0.909	1.06
$BaCl_2$	6.41	(b) 0.858	
KCl	15.41	(a) 75.1	1.22
KCl	6.41	(b) 61.5	

From his observations Freundlich concludes that the precipitation values of electrolytes for colloids of different concentrations bear a constant ratio to each other as shown in the last column in Table I. Recently, Kruyt and van der Spek[2] showed that this rule does not hold when particular care is taken in the preparation of the colloids so that comparable results are obtained. This is shown by the results given in Table II, in which the ratio a/b shows wide variation with different electrolytes. Arsenious sulphide colloids were used.

[1] Zeit. phys. Chem., **44**, 129 (1903).

[2] Zeit. Kolloidchemie, **25**, 11 (1919).

TABLE II

Electrolyte	Concentration of colloid, millimoles per 1	Precipitation value, millimoles per 1	$\frac{a}{b}$
KCl	18.00	(a) 52.0	1.00
KCl	5.60	(b) 52.0	
$BaCl_2$	16.00	(a) 1.16	1.54
$BaCl_2$	5.30	(b) 0.75	
$KAl(SO_4)_2$	13.38	(a) 0.302	2.08
$KAl(SO_4)_2$	4.60	(b) 0.145	

In some experiments on the precipitation of negative mastic emulsion Neisser and Friedemann[1] showed that the precipitation value of salts with univalent cations is less the more concentrated the emulsion while with divalent and trivalent cations the precipitation value decreases slightly as the concentration of the colloid decreases.

Odèn[2] found that the precipitation value of potassium chloride increases and of sodium chloride decreases with decreasing concentration of colloidal sulphur.

Mukhopadhyaya[3] carried out some experiments with colloidal arsenious sulphide which indicate that the precipitation value of sodium chloride increases with decreasing concentration of colloid. This result was confirmed for both potassium and sodium chloride by the investigations of Kruyt and van der Spek,[4] Bach[5] and Burton[6] and Bishop. Kruyt and van der Spek showed further that the precipitation value of barium chloride decreases slightly and of $KAl\ (SO_4)_2$ decreases greatly as the concentration of the colloid decreases. In explanation of these observations they state: "For a correct understanding of the relationship between colloid concentra-

[1] München. med. Wochenschr., **51,** 827 (1904). Cf. Bechold: Zeit. phys. Chem., **48,** 385 (1904).

[2] "Der kolloide Schwefel," (1912).

[3] Jour. Am. Chem. Soc., **37,** 2024 (1915).

[4] Zeit Kolloidchemie, **25,** 3 (1919).

[5] Jour. Chim. phys., **18,** 52 (1920).

[6] Jour. Phys. Chem., **24,** 701 (1920). See also Burton and MacInnes: Ibid., **25,** 517 (1921).

tion and precipitation value we have to recognize two opposing tendencies. Since a smaller amount needs to be adsorbed for reaching the same adsorption value in the case of a dilute colloid, it follows that a smaller amount of electrolyte is required for a dilute colloid than for a more concentrated one. On the other hand, since the probability of collision of the particles is smaller for the colloid of lesser concentration, the dilute colloid requires a greater amount of electrolyte than the concentrated so that the lesser probability of collision is compensated by an increased probability of coalescence, and the same coagulation can result in the same time."

"By diluting a colloid the number of particles is decreased; on this account a smaller amount of electrolyte is adsorbed and so we need to add a smaller amount of electrolyte. According to our hypothesis, this effect is most marked with $Al^{\cdot\cdot\cdot}$, less with $Ba^{\cdot\cdot}$ and very small with $K^{\cdot}$. At the same time the probability of collision is less and in order to compensate for this, we must increase the probability of coalescence, that is, the charge on the particles must be lowered. It appears from the above considerations that a considerable amount of $K^{\cdot}$, less $Ba^{\cdot\cdot}$ and only a trace of $Al^{\cdot\cdot\cdot}$ is necessary for a smaller lowering of the charge.

"By dilution of a colloid one should expect the precipitation value of $K^{\cdot}$ to increase for, even though the smaller number of particles requires a lesser adsorption, the amount of this decrease is very small compared to the entire concentration of electrolyte added. For lowering the charge, however, a considerable amount of electrolyte is necessary and this last named influence predominates with $K^{\cdot}$.

"With $Al^{\cdot\cdot\cdot}$ one should expect the precipitation value to decrease with dilution of the colloid since we require much less electrolyte for the first mentioned influence. The second influence requires but a small amount of electrolyte so that the former overbalances the latter.

"With $Ba^{\cdot\cdot}$ one should expect that the precipitation value would not be changed appreciably with the dilution of the

colloid, since the amount of electrolyte required for the first influence is less than with $K^{\cdot}$ while that for the second is greater than with $Al^{\cdot\cdot\cdot}$; and the two approximately compensate each other."

In support of the above explanation Kruyt and van der Spek showed that increasing the size of the particles of colloidal As_2S_3 by boiling, increased the precipitation value considerably for KCl, very little for $BaCl_2$ and decreased it for $KAl(SO_4)_2$.

Experiments carried out by Kruyt and van der Spek[1] on the precipitation of colloidal hydrous ferric oxide showed that the precipitation value of all electrolytes decreased with dilution of the colloid.

Recently Burton and Bishop[2] have studied the effect of concentration of colloid on the precipitation value of electrolytes, using colloidal arsenious sulphide, copper and mastic. From their results they deduce the following laws: "I. For univalent ions the concentration of ion necessary to produce coagulation increases with decreasing concentration, this increase being very rapid with low concentrations of the colloid. II. For divalent ions the concentration of ion necessary to produce coagulation is almost constant and independent of the concentration of the colloid. III. For trivalent ions the concentration of ion necessary to produce coagulation varies almost directly with the concentration of the colloid."

In explanation of their observations Burton and Bishop merely state that several elements possibly enter into the process of coagulation, one of which predominates with univalent and another with trivalent ions. They suggest that the ion having the same charge as the colloid may influence the precipitation value; but do not state how this influence can account for the laws quoted above.

[1] Loc. cit.

[2] Loc. cit.

Experimental

In some preliminary experiments with several colloids, the precipitation values of all electrolytes were found to decrease with decreasing concentration of colloid. These results indicated that the laws formulated by Burton and Bishop are not general and led to additional experiments that will now be described.

Experiments with Colloidal Hydrous Chromic Oxide

Preparation of Colloid.—Colloidal hydrous chromic oxide was prepared by peptizing the precipitated oxide with chromic chloride and dialyzing out the excess chloride in the hot according to the method decsribed by Neidle.[1] The concentration of this colloid was determined and from it other colloids were prepared by diluting definite portions.

Determination of Precipitation Values.—The approximate precipitation value was first found after which the exact value was determined using a mixing apparatus similar to that described in earlier investigations.[2] In the outer compartment of this apparatus were placed 20 cc of colloid and in the inner compartment a quantity of electrolyte of suitable concentration diluted to 40 cc. After mixing the solutions they were transferred to a cylindrical vessel and allowed to stand 24 hours before examining for complete precipitation. A series of experiments carried out in the immediate region of the precipitation value established this value with a considerable degree of accuracy. The results are given in Table III and are shown graphically in Fig. 1. The concentration of the several colloids is expressed in percent, taking the most concentrated as 100%. The precipitation values are given in milliequivalents of electrolyte per liter. The curves shown in Fig. 1 were obtained by plotting concentration against ratio of each precipitation value for a given electrolyte to that of the strongest colloid. The curve for $K_4Fe(CN)_6$ coincides so nearly with that for $K_3Fe(CN)_6$ that the former is omitted.

[1] Jour. Am. Chem. Soc., **39**, 71 (1907).
[2] Weiser and Middleton: Jour. Phys. Chem., **24**, 48 (1920).

TABLE III

Precipitation of Chromic Oxide Colloids

Concentration of colloid	Precipitation values of			
	KSCN	K_2SO_4	$K_3Fe(CN)_6$	$KFe_4(CN)_6$
100% (3.72 g per 1)	45.6	2.40	1.800	1.600
75%	36.0	1.83	1.347	1.190
50%	29.0	1.60	0.907	0.816
25%	22.9	0.63	0.413	0.385
10%	15.6	0.33	0.173	0.175

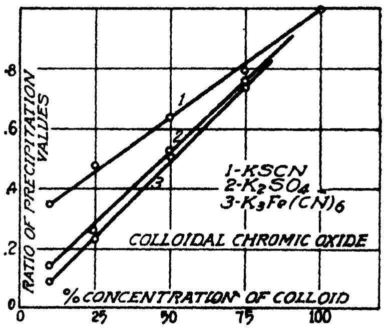

Fig. 1

Experiments with Colloidal Prussian Blue

Preparation of Colloid.—Prussian blue was prepared by mixing suitable solutions of potassium ferrocyanide and ferric ammonium sulphate. The precipitate so obtained was peptized with potassium ferrocyanide and dialyzed for one week. The colloid still contained an excess of ferrocyanide but this was unobjectionable for the purpose of the experiments.

Determination of Precipitation Values.—Precipitation values were determined exactly as described for colloidal chromic oxide. The values for KCl are not very accurate but the observations were conclusive that the values decrease with decreasing concentration of the colloid. The results are given in Table IV and are shown graphically in Fig. 2.

TABLE IV

Precipitation of Prussian Blue Colloids

Concentration of colloid	Precipitation value of		
	KCl	$BaCl_2$	$AlCl_3$
100% (8 g per 1)	89.6	4.25	2.200
75%	87.5	3.33	1.625
50%	85.4	2.75	1.125
25%	81.2	2.16	0.500
10%	77.1	1.67	0.208

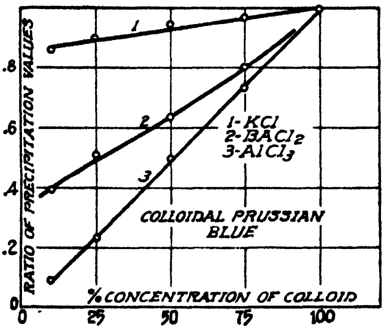

Fig. 2

Experiments with Colloidal Hydrous Ferric Oxide

Preparation of Colloid.—Colloidal hydrous ferric oxide was prepared by hydrolysis of ferric acetate as described in detail in a former communication.[1]

Determination of Precipitation Values.—Precipitation values were determined as described above except that 20 cc of colloid was mixed with an equal amount of electrolyte. The results are given in Table V and are plotted in the usual way as shown in Fig. 3.

[1] Weiser: Jour. Phys. Chem., **24**, 277 (1920).

TABLE V
Precipitation of Ferric Oxide Colloids

Concentration of colloid	Precipitation values of		
	$KBrO_3$	K_2SO_4	$K_4Fe(CN)_6$
100% (1.7 g per 1)	40.1	0.68	0.57
50%	34.4	0.41	0.30
25%	28.0	0.25	0.16
12.5%	25.0	0.16	0.08

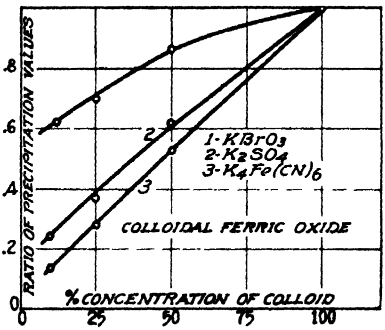

Fig. 3

With each of the three colloids so far considered, the precipitation values for all electrolytes were found to decrease as the concentration of the colloids was decreased. Some experiments were next carried out on colloidal arsenious sulphides using the same general method of procedure.

Experiments with Colloidal Arsenious Sulphide

Preparation of Colloid.—Colloidal As_2S_3 was prepared by passing hydrogen sulphide into a suspension of As_2S_3 until peptization was complete, removing excess hydrogen sulphide with a current of hydrogen.

Determination of Precipitation Values.—Precipitation values were determined by the method of procedure outlined under the experiments with colloidal chromic oxide. The mixtures were tested for complete precipitation after three hours by filtering into Nessler tubes and examining for the presence or

absence of the bluish coloration characteristic of the very dilute colloid. The results are given in Table VI and are shown graphically in Fig. 4. In accord with the observations of other investigators, it will be noted that the precipitation value of KCl increases as the concentration of the colloid is decreased.

TABLE VI
Precipitation of Arsenious Sulphide Colloids

Concentration of colloid	Precipitation values of		
	KCl	$BaCl_2$	$AlCl_3$
100% (6.24 g per 1)	68.3	1.940	0.513
75%	68.3	1.877	0.473
50%	70.0	1.800	0.380
25%	76.7	1.733	0.333
10%	80.0	1.683	0.260

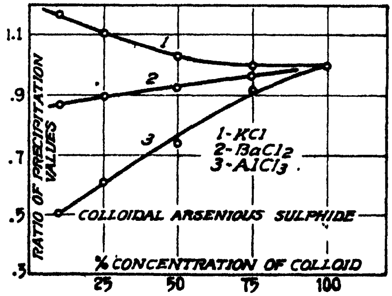

Fig. 4

The Effect of Time on the Precipitation Value.—In determining the precipitation values it is necessary to adopt a definite time limit since a concentration of electrolyte that will not cause complete coagulation in two hours, say, may do so in a longer time. Kruyt and van der Spek have pointed out that diluting a colloid affects the precipitation value of electrolytes by decreasing the chances of collision. It would seem that this effect might be compensated by increasing the time of standing. Accordingly, the following experiment was tried: It

was found that 10 cc of colloidal As_2S_3 containing approximately 5 g per liter was precipitated completely in 2 hours by the addition of 2.65 cc of N/2 KCl diluted to 10 cc. This amount of electrolyte was added to 10 cc of colloid that was one-fourth as strong as the original. Although, a considerable amount was precipitated in 2 hours, coagulation was not complete even after 3 weeks. The result of this experiment shows that the decreased chance of collision of particles produced by diluting colloidal As_2S_3 cannot be compensated by adding an amount of KCl sufficient to precipitate the undiluted colloid and allowing to stand a reasonable time.

The Influence of the Stabilizing Ion on the Precipitation Value.—The precipitation value of an electrolyte for a given colloid is that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion of the electrolyte added. Thus, the precipitation value of KCl for colloidal As_2S_3 is such a concentration that the adsorption of $K^{\cdot}$ is sufficient to neutralize the combined adsorption of HS' and Cl'.[1] Obviously, the greater the adsorption of the stabilizing ion of an electrolyte, the greater will be its precipitation value. The effect of the stabilizing ion is particularly marked in the precipitation of colloidal As_2S_3 with different salts of potassium as shown by the experiments recorded in Table VII. The adsorption values were determined by mixing equal portions of colloid and electrolyte and examining for complete precipitation as described above.

TABLE VII

The Influence of the Stabilizing Ion on the Precipitation Value for Colloidal As_2S_3

Concentration of colloid	Precipitation values of		
	KCl	K_2SO_4	$K_4Fe(CN)_6$
100% (5 g per l)	33.2	43.5	71.2
25%	41.8	....	93.7

[1] Weiser: Jour. Phys. Chem., 25, 665 (1921).

From the results recorded in Table VII it is evident that the greater the valence of the stabilizing ion, the greater is the precipitation value of the potassium salt. This is accounted for by the fact that the ion of highest valence is usually the most strongly adsorbed and so has the greatest stabilizing influence. The results show further that the increase in precipitation value with dilution of colloid is greater, the greater the valence of the stabilizing ion.

Discussion of Results

Earlier in this paper attention has been called to the generalizations of Burton and Bishop. According to these investigators, the precipitating action of univalent ions increases and of trivalent ions decreases with decreasing concentration of colloid: while that of divalent ions is almost independent of the concentration of the colloid. The results of the above series of experiments show conclusively that these rules are by no means general. Thus with colloidal chromic oxide, Prussian Blue and ferric oxide, the precipitation value of all electrolytes studied decreases as the concentration of the colloid decreases, irrespective of the valence of the precipitating ion. With colloidal As_2S_3 the precipitation value of $K^{\cdot}$ increases and of $Al^{\cdot\cdot\cdot}$ decreases as the concentration of the colloid decreases, in accord with Burton and Bishop's rules. However from the slope of the curve in Fig. 4 it is obviously incorrect to say that the precipitating action of divalent $Ba^{\cdot\cdot}$ is independent of the concentration of the colloid; this is no more true of $Ba^{\cdot\cdot}$ than of $K^{\cdot}$.

Kruyt and van der Spek conclude from their experiments that two factors determine the effect of dilution of a colloid on the precipitation value of electrolytes: First, the decreased number of particles which decreases the amount of electrolyte necessary to cause sufficient adsorption to lower the charge on the particles to the point where agglomeration takes place; and second, the increased distance between the particles which decreases the chance of collision. This latter effect must be compensated by greater lowering of the charge,

hence by the addition of more electrolyte. Since these two factors have opposite effects on the precipitation value, it is only necessary to assume the predominating influence of one or the other in order to account for the results in a given case. Thus, Kruyt and van der Spek assume that the effect which results from changing the chance of collision of particles predominates in the precipitation of colloidal arsenious sulphide with $K^{\cdot}$; while the effect which follows from changing the amount that must be adsorbed predominates in the precipitation of colloidal hydrous ferric oxide with Cl': "Consistent with our theory of the mechanism of the process of coagulation, the results obtained show that in the case of colloidal hydrous ferric oxide, the effect which follows from changing the amount adsorbed is the greater at least for all precipitating ions investigated. This is understood when one considers that the ferric oxide possesses lyophile properties while arsenious sulphide is a pure lyophobe colloid."

Although both of the factors recognized by Kruyt and van der Spek unquestionably have an influence in determining the effect on the precipitation value of changing the concentration of the colloid, it would seem that these factors in themselves are inadequate to account for all the experimental results. As mentioned above these investigators attribute the difference in the behavior of colloidal arsenious sulphide and hydrous ferric oxide, with univalent precipitating ions to the fact that the hydrous oxide possesses lyophile properties not possessed by the sulphide. Such a suggestion without further comment is always of doubtful value and particularly so in this case in view of the fact that experiments with mastic emulsion[1] lead to results similar to those with colloidal As_2S_3 although mastic possesses more lyophile properties than ferric oxide. Furthermore, if the decreased chance of collision is the predominating factor that prevents a weaker colloidal As_2S_3 from coagulating in a given time in the presence of enough KCl to coagulate a stronger colloid, it would seem that com-

[1] Neisser and Friedemann: Loc. cit.; Burton and Bishop: Loc. cit.

plete coagulation of the weaker colloid should result if sufficient time were allowed. We have seen, however, that enough KCl to precipitate in 2 hours a colloid containing 5 g per liter will not precipitate a colloid one-fourth as strong in 3 weeks. Other observations indicate that Kruyt and van der Spek attach too much importance to the decreased chance of collision of the particles resulting from dilution of colloids. Thus we have found that the precipitation concentration varies almost directly with the concentration of the colloid in case the precipitating ion is of high valence, a relationship that was pointed out by Burton and Bishop. The same thing is indicated by certain experiments of Kruyt and van der Spek with colloidal hydrous ferric oxide. Thus with concentrations of 2.89, 2.17, 1.44 and 0.72 grams of Fe_2O_3 per kilogram of colloid the precipitation values of Na_2SO_4 were found to be 2.05, 1.58, 1.09 and 0.58 millimoles per liter, respectively.

That the theory of Kruyt and van der Spek should be inadequate in certain respects might be expected in view of the fact that these investigators concerned themselves only with the precipitating ions of electrolytes disregarding entirely the effect of adsorption of the stabilizing ions having the same charge as the colloid. If there is no adsorption of the stabilizing ion and if the adsorption of the precipitating ion is very great we might expect the precipitation concentration to vary almost directly with the concentration of the colloid. On the other hand if the stabilizing ion is adsorbed, a greater concentration of precipitating ion will be required to produce coagulation. This effect will be more pronounced the greater the dilution of the colloid since the decreased chance both of collision and coalescence will combine to render the colloid proportionately more stable so that proportionately more of the precipitating ion must be added for complete precipitation. These conclusions are in accord with the experimental results.

With electrolytes having multivalent precipitating ions, the influence of the stabilizing ion is frequently very small since the adsorption is so slight at the very low precipitation

concentration. Under these conditions the precipitation value decreases to a greater or lesser extent as the concentration of the colloid decreases as indicated by the figures in the experimental part of this paper. As might be expected, the greater the valence of the precipitating ion and hence, the lower the precipitation value, the more nearly we find the precipitation concentration varying directly with the concentration of the colloid.

With electrolytes having univalent precipitating ions the precipitation value is usually quite large. Although this is generally considered to be due to weak adsorption of the precipitating ion, the adsorption of the stabilizing ion cannot be disregarded at the high concentration necessary for coagulation. In fact if the adsorption of the two ions is of the same order of magnitude, both may be taken up fairly strongly and a high precipitation value will result. In a former communication[1] evidence was obtained which seemed to indicate that K. is fairly strongly adsorbed by As_2S_3, the high precipitation value of KCl for this colloid arising from appreciable adsorption of Cl′. In the same paper it was pointed out that the high precipitation value of KCl for colloidal hydrous ferric oxide was due to weak adsorption of the precipitating ion, the stabilizing ion having much less effect than with colloidal As_2S_3. The results in Table VII emphasize the marked influence of the stabilizing ion on the precipitation values of potassium salts for colloidal As_2S_3. Similar experiments[2] with colloidal Fe_2O_3 show that the effect of the stabilizing cations is much less marked, the precipitation value of NaCl being 9.25 while that of $BaCl_2$ is but 9.64. In general it may be said that the adsorption of the stabilizing ion varies widely but is never negligible if the electrolytes precipitate only in high concentration as is usual with electrolytes having univalent precipitating ions. This adsorption of the ion having the same charge as the colloid renders the latter proportionately more stable and

[1] Weiser: Jour. Phys. Chem., **25**, 665 (1921).

[2] Freundlich: "Kapillarchemie," 352 (1909).

proportionately more of the precipitating ion is required for coagulation than in those cases where the influence of the stabilizing ion is negligible. Under these conditions we may expect the precipitation value to fall off much less sharply or even to increase as the concentration of the colloid decreases. Thus we note that as the colloids are diluted the precipitating action decreases much less sharply with salts having univalent precipitating ions than with salts having divalent or trivalent precipitating ions. And in the case of colloidal As_2S_3 where the influence of the stabilizing ion is particularly marked, the precipitation concentration actually increases as the colloid concentration is reduced, the increase being greater the greater the valence of the stabilizing ion.

Kruyt and van der Spek showed that boiling colloidal As_2S_3 increased the precipitation value of KCl for the colloid. Raising the temperature of this colloid may affect it in several ways. Thus it may change, (1) the peptizing action of the solvent, (2) the concentration of the stabilizing ions, HS', S'' or AsS_3''', (3) the adsorption of the stabilizing ions, (4) the size of the particles and (5) the extent of hydrolysis of the sulphide. Until we know more about how the colloid is changed by boiling, it is impossible to say how boiling should affect the precipitation value of a given electrolyte.

Summary

The results of this investigation may be summarized briefly as follows:

(1) An investigation has been made of the precipitation of colloidal chromic oxide, Prussian Blue, ferric oxide and arsenious sulphide of different concentrations, using electrolytes with precipitating ions of different valence.

(2) With colloidal chromic oxide, Prussian Blue and ferric oxide, the precipitation values of all electrolytes decrease as the concentration of the colloid is lowered, irrespective of the valence of the precipitating ion; but the decrease is least marked with electrolytes having univalent precipitating ions. With colloidal arsenious sulphide, the precipitation

value of electrolyes with univalent precipitating ions increases as the concentration of the colloid is decreased.

(3) The manner in which the precipitation value of an electrolyte varies with the concentration of colloid is determined to a large extent by the relative adsorbability of the precipitating ion and the stabilizing ion.

(4) If the adsorption of the stabilizing ion of an electrolyte is negligible and the adsorption of the precipitating ion is very large, the precipitation value varies almost directly with the concentration of the colloid. This condition may be realized experimentally with electrolytes having trivalent and tetravalent precipitating ions which precipitate in extremely low concentration.

(5) If the adsorption of the stabilizing ion of an electrolyte is appreciable, the precipitation value is increased. This effect is more pronounced the greater the dilution of the colloid, since the decreased opportunity both of collision and coalescence of particles combine to render the colloid proportionately more stable so that proportionately more of the precipitating ion must be added for complete coagulation. The influence of adsorption of the stabilizing ion is more marked with electrolytes having univalent precipitating ions which precipitate only in very high concentration. Under these conditions the precipitation value falls off much less sharply than under the conditions given in (4) and may even increase as the concentration of the colloid is decreased.

(6) Burton and Bishop's laws covering the variation in coagulative power of ions with the concentration of the disperse phase, have been shown to be quite limited in their applicability.

(7) Kruyt and van der Spek's theory of the nature of the process of coagulation is inadequate since it fails to take into account the influence of the stabilizing ions of electrolytes.

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A QUICK-ACTING HYDROGEN ELECTRODE

BY P. J. MOLONEY

When the hydrogen electrode is used for determining the acidity (hydrogen-ion concentration) of solutions, it is assumed that the platinum is in equilibrium with hydrogen at atmospheric pressure; the absorption of hydrogen by platinum, however, is far from instantaneous, and if the electrolyte contains dissolved oxygen or an oxidizing agent, the concentration of hydrogen in the platinum will be lower than that assumed, and the conclusions drawn from the E. M. F. measurement will be erroneous. When working with synthetic solutions this source of error can be avoided by using pure chemicals and working in the absence of air; with blood, sera, etc., the method adopted is to reduce the oxidizing substances, if any are present, by the continued action of the hydrogen and the platinum of the electrode. In the cells of Hasselbalch, Clark, Hildebrand,[1] etc., this result is brought about by shaking the liquid with hydrogen gas and a fairly large electrode of platinized platinum sheet. In the cell known as Michaelis', shaking must be avoided altogether, and the electrode previously saturated with hydrogen is allowed merely to touch the surface of the liquid; there is here no attempt to remove oxidizing agents from the bulk of the solution, only a small film immediately surrounding the electrode is reduced and if the apparatus be jarred, fresh solution is brought in contact with the platinum, and the E. M. F. changes at once.

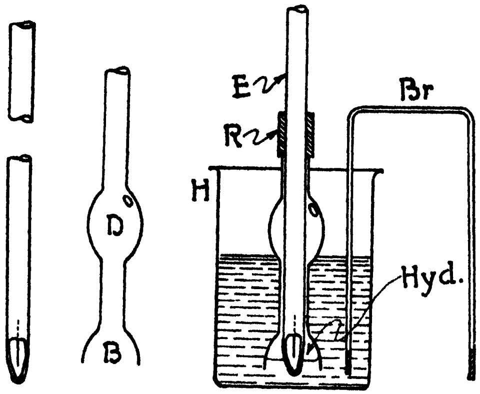
During the past year I have had occasion to make hundreds of these determinations, and after much experience with the usual forms, have devised a hydrogen electrode which combines the advantages of both types referred to above. In this new apparatus, the platinized platinum wire is surrounded

[1] Illustrations of the common forms are given in W. M. Clark: "The Determination of Hydrogen Ions," 138 (1920).

by a drop of the liquid to be measured which is held in position by capillarity and is surrounded by an atmosphere of hydrogen. Oxidizing agents are thus removed from only a small quantity of liquid, and as in Michaelis' form equilibrium is rapidly attained; on the other hand, as all the liquid that can come in contact with the platinum is reduced, jarring is without effect, and the advantages of Clark's form are retained.

This electrode has been in constant use for several months for determining the acidity of broths used in the culture of bacteria; as the results agree with those obtained from a cell of the Clark form, while the manipulation is simpler and very much quicker, I thought that a description of the apparatus might prove of general interest.

Electrode and Loop.—The electrode (see Fig. 1) consists of a platinum wire sealed into a glass tube of 4 mm diameter; 4 mm of the end of the wire is exposed, contact is made through



Figs. 1–3

mercury in the usual way. On either side of the wire there is sealed to the glass tube a small piece of glass rod, 1 mm in diameter; these two are joined at the bottom to form a loop, as shown in the figure; the length of this loop should be 9 to 10 mm, it is to hold the drop of liquid in which the platinum is immersed. The glass rods should be sealed well towards the edge of the tubing, but should not extend beyond the sides,

so that there may remain a gap of at least one-half millimeter between the platinum wire and each side of the loop. When the glass-blowing is finished, the wire is platinized in the usual way.

Bell-Tube.—The electrode has been used with several types of holders, a convenient form is shown in Fig. 2; it is made from a piece of tubing just large enough to slip over the electrode tube without binding. A bulb D is blown near the lower end of the tube, and a small hole about three-quarters way up the bulb; a bell B is then blown at the bottom of the tube; the distance from the bottom of the bulb to the top of the bell should be about one centimeter.

Operation.—The electrode tube E is slipped into the bell tube H, and a piece of rubber tube R fitted over the joint so that the relative position of electrode and bell can be easily adjusted. The electrode is pulled up until wire and loop are within the bulb, and the whole is immersed in the liquid to be measured (which may be in an open vessel) until the tube connecting bulb and bell is filled. The apparatus is held in this position by means of a clamp, and the electrode is pushed down until wire and loop are in the bell; hydrogen is then introduced under the bell, and the electrode adjusted until the wire is surrounded by hydrogen, while the lower end of the loop dips into the main body of liquid in the bell (see Fig. 3). Connection between the main body of the liquid and the calomel electrode is made by a bridge Br, consisting of a capillary filled with saturated potassium chloride solution, both ends being plugged with cotton wool; when not in use, both ends of this bridge tube are left standing in tubes filled with the potassium chloride solution.

In making duplicate readings, when the solution to be measured is exposed to the air in an open vessel, it is safer not to renew the liquid in the loop (at least not more than once or twice) by merely lowering and raising the electrode; the electrode should be pulled up into the bulb, and the hydrogen renewed, as in the first instance.

Summary

(1) A new form of hydrogen electrode has been described in which the electrolyte is held by capillarity in a glass loop surrounding a platinized platinum wire, and surrounded in turn by an atmosphere of hydrogen.

(2) Equilibrium, as indicated by constant E. M. F., is reached very rapidly, usually in less than one minute; and the readings agree with those of a Clark electrode to within one millivolt.

(3) The electrode can be rapidly washed and sterilized.

(4) The liquid to be measured can be contained in an open vessel; but if it is proposed to measure electrolytes whose acidity depends on the presence of dissolved carbon dioxide, a closed vessel must be employed, such as a Michaelis' V tube, or a modification of Walpole's or Barendrecht's apparatus. With the open vessel it is obvious that the carbon dioxide would rapidly pass from the drop into the surrounding hydrogen, and the acidity as measured would be less than that of the original liquid.

I am glad of this opportunity to express my thanks to Professor J. G. Fitzgerald for the facilities he has placed at my disposal, and the continued interest he has taken in the progress of the work.

Research Division, Connaught Laboratories
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June 1921

NEW BOOKS

The Volatile Oils. *By E. Gildemeister and F. Hoffmann. Vols. I and II. 23 × 16 cm; pp. xiii + 677 and xx + 686, respectively. New York: John Wiley and Sons, 1913 and 1916. Price: $7.50 each.*—Through some mistake these volumes were not reviewed when they first appeared, perhaps because it was thought that physical chemists would not be interested in them. The first volume deals with: historical introduction; production of flower perfumes by extraction, enfleurage, and maceration; principal constituents of volatile oils, natural and artificial perfumes; the examination of volatile oils. In the second volume the oils are discussed under the divisions: *Chlorophyceae; Eumycetes; Embrophyta asiphonogama; Embrophyta siphonogama.* The first three divisions take up five pages and the last division over six hundred and forty pages. A third volume will complete the work.

Among the interesting things to be noted is that the crystalline deposits from volatile oils were, in the old days, usually considered as identical with ordinary camphor because, like it, they were volatile, soluble in alcohol and fatty oils, and burned with a smoky flame (I, 77). As early as 1837 Berzelius protested against applying the term camphor to all solid volatile oils and he substituted the word stearoptene. The misuse of the word camphor continues, however, to this day as is shown by the terms, cedar camphor, cubeb camphor, juniper camphor, etc.

Nowadays saffron is practically unknown in the United States, though it is used extensively as a flavoring for rice in Italy. "In the literature of antiquity saffron is frequently mentioned among the spices, also as medicament and dyestuff. During the Arabian period it was cultivated, especially in Persia and Spain. Its introduction into Western Europe as far as England was no doubt assisted by the crusades (I, 105). In the commerce with the Levant, saffron was one of the most costly spices and played an important rôle . . . So important did the commerce in saffron become during the Middle Ages that the traders in spices of some of the larger German cities united under the name of *Safranzunfte* to special corporations."

Pepper is another substance which has fallen from its former high estate (I, 114). "Into Western Europe pepper was likewise introduced at an early date. The quantities, in which it was imported in spite of its high price at the beginning of the fifth century, become apparent from the statement that the Roman Emperor, Honorius, paid a tribute of 3000 lbs. of pepper to Alaric, King of the Visigoths, in 408 while the latter was besieging Rome. Pepper retained its high price late into the Middle Ages. Hence it was used in place of the noble metals in the payment of tribute, taxes, rent, duty, and ransom; as gifts and as objects of bequest. Among the presents made to the popes by the Eastern and Western Emperors, pepper is usually enumerated first among the costly spices. . . The increasing demand for pepper and the high price paid therefor constituted not the least of the motives for the search for an all-water route to the East Indies."

The volatile oils may be extracted from flowers by: extraction with volatile solvents; extraction with non-volatile solvents (fats) without the aid of heat

(enfleurage); extraction with non-volatile solvents (fats) with the aid of heat (maceration). Extraction with volatile solvents is applied to roses, Parma and Victoria violets, orange blossom, jasmine, tuberose, jonquil, cassie, and mignonette; occasionally to carnations, lily of the valley, heliotrope, elder flowers, stock, narcissus, and mimosas. Enfleurage yields the best results with jasmine, tuberose, jonquil, lily of the valley, and mignonette. The process of maceration is applied to rose, orange flower, violet, cassie, and lily of the valley. Some flowers, e. g., rose, cassie, and violet, can be treated equally well either with volatile solvents or with warm fats. It has been known for a long time that jasmine and tuberose, when thus treated, give an unsatisfactory yield, whereas the enfleurage process gives good returns. Attention was first called to this fact by Passy, who gave the following explanation (I, 246) for this difference in behavior of the several flowers.

"Flowers can be divided into two classes. In one, to which rose and orange flower belong, the flowers contain their perfume ready made. In the other class, to which jasmine and tuberose belong, the flowers contain either no ready-made volatile oil or but little thereof. These, however, continually produce perfume as part of the life process of the cells. If the flower be killed by petroleum ether or hot fat, the life process naturally ceases and, with it, the formation of volatile oil. If, however, the cut flower be placed over fat, it continues to live for a long time and to emanate odors which in the enfleurage process are absorbed by the fat."

When Hesse tested this hypothesis experimentally, he arrived at the surprising result that, in the case of jasmine, the enfleurage process yields ten times the amount of oil yielded by the extraction with volatile solvents. In the case of tuberose the proportion is even greater. Hence the conclusion is justified that in the case of the jasmine and the tuberose the production of odoriferous substances continues during the process of enfleurage. For other flowers this does not hold true. According to Hesse and Zeitschel, 1000 kilos of orange blossoms yield only 100 grams of volatile oil when submitted to the enfleurage process, whereas maceration yields 400 grams and distillation with steam 1200 grams of oil, of which about 400 grams are dissolved in the aqueous distillate. The question of the relation between the nature of the volatile oil and the period of production is apparently still unanswered.

Turpentine oil is miscible in all proportions with absolute alcohol and is practically non-miscible with aqueous alcohol containing 18.4 percent of alcohol by volume (II, 17). When ascaridol is suspended in water in presence of colloidal platinum, it takes up four atoms of hydrogen with such rapidity that the inflow of hydrogen must be regulated in order to prevent too great an evolution of heat (II, 364). The clever way in which the Chinese adulterate cassia oil is worth noting (II, 431). The firm of Schimmel and Co. claim that the German oil of rose, made from flowers grown at Miltitz near Leipzig, is far superior to the Bulgarian product owing to the extra care used in the extraction. Although the stearoptene content of the German product is high, the odor is twice as intense (II, 558). It is interesting to learn that the almond trees which yield bitter almonds show no constant botanical differences from those which produce sweet almonds. Probably all almond trees originally produced bitter almonds, and it may be that continuous cultivation resulted in the sweet variety

(II, 577). As might have been expected, the eutectic mixture of the two isomeric semicarbazones of the citral from lemon-grass oil was for some years considered as a third modification (II, 196).

In the second volume, p. 27, there is quite a discussion of the action of air and light on turpentine oil. Engler "showed that the action of atmospheric oxygen or pure oxygen on turpentine oil results in the formation of a peroxide-like oxidation product, $C_{10}H_{16}O_4$. This can give off one-half of its oxygen, whereas the other half remains with the oil. He confirmed the observation, previously made by Berthelot, that one mol of turpentine oil absorbs four atoms of oxygen, of which two are readily removed. Thus far, however, the isolation of either the compound $C_{10}H_{16}O_4$ or $C_{10}H_{16}O_2$ has not been accomplished. When absolutely dry turpentine oil is activated, neither hydrogen peroxide nor ozone results. Turpentine oil activates oxygen most rapidly at 100°. Above this temperature no active oxygen is formed since it is used up in the oxidation of turpentine oil. 1 cc of turpentine oil can activate 100 cc of oxygen at 100°. The turpentine oil charged with oxygen, whether moisture be present or not, is capable of transmitting oxygen to substances which are not directly oxidizable by atmospheric oxygen. Thus, as has already been pointed out, iodine is liberated from potassium iodide. Indigo solution is bleached and arsenious acid is oxidized to arsenic acid. In the dark, activated turpentine oil retains its properties for years. These oxidation phenomena and the same changes in the turpentine oil take place more rapidly when warmed air saturated with moisture is passed through the oil."

A phenomenon for which there is no explanation at present is the fact that cinnamyl acetate retards the oxidation of the cinnamic aldehyde which is the essential ingredient both of cassia oil and of cinnamon oil (II, 430). "A very old cassia oil, containing 77.7 percent of aldehyde, was exposed for a year in a shallow dish, covered with perforated filter paper, in a place where warmth, light, and air had free access. After the expiration of this time, the cinnamic acid content, which had amounted to 0.7 percent in the original oil, had increased to 8.5 percent. A real resinification had not taken place, for the distillation residue was but little greater at the end of this period than at the beginning. Under like conditions, pure cinnamic aldehyde would soon have been changed to lumps of cinnamic acid."

Wilder D. Bancroft

Metallography. Part II. The Metals and Common Alloys. *By Samuel L. Hoyt. 23 × 15 cm; pp. ix + 462. New York: McGraw-Hill Book Company, 1921. Price: $5.00.*—In this volume the author discusses the more important metals and alloys, taking up the constitution and microstructure, the physical and mechanical properties for different conditions of heat and mechanical treatment, the effects of the impurities commonly present and the uses. The chapters are entitled: the pure metals; white metal alloys; light metal alloys; brasses and bronzes; steel and cast iron; special steels.

This is a valuable book, having many good points and only a few weak ones. On p. 18 the author calls attention to the fact that the amorphous phase theory was developed to account for the high tensile strength of hard-drawn copper and other metals, and yet we can get similar strengths by electrolytic deposition of copper under conditions which seem to exclude the formation of amor-

phous metal. On p. 23 the author rather implies that the ancients had the art of hardening copper without alloying it. If he really believes this, he should have given the evidence for it. He apparently does not realize how hard this myth dies. On page 291 the existence of Cu_2Zn_3 as a definite chemical compound is postulated, apparently because some other people have done the same. In a book of this sort a problem like this should be discussed and some evidence should be given for the conclusions adopted. The situation in regard to martensite is still very vague, pp. 115, 183. The author inclines to the view that it is a metastable, allotropic, modification of the γ solid solution, which is not the view taken by Upton, and which seems improbable until somebody has found some similar change somewhere. The analogy with α tridymite and β tridymite, does not seem satisfactory.

The author objects strongly on p. 175 to the conception that "steel of eutectoid composition is supposed to form first martensite, then troostite, and then pearlite, by change in the iron from γ to β to α and then finally the splitting up into α iron and Fe_3C." He says that this conception disregards completely the laws of heterogeneous equilibria and the phase rule. That is a terrible indictment and disposes completely of the offending view if true; but the reviewer finds himself quite unable to agree with the author's reasoning and he is unimpressed by the statement that a brine solution is one of salt in water and not one of salt in ice. The utterance of a platitude which has no bearing on anything is a familiar line of argument but not a convincing one.

On p. 186 the author adopts Campbell's view that the molecular weight of a carbide can be deduced without error from the molecular weight of the hydrocarbon formed from it.

On p. 254 the author gives a diagram by Sieverts showing increasing solubility of hydrogen in iron with rising temperature. It seems to the reviewer that some discussion of this would have been desirable. For hydrogen to be more soluble in iron with rising temperature, it must dissolve with absorption of heat. At ordinary temperatures gases dissolve in liquids with evolution of heat and we ascribe much of the heat effect to the heat of liquefaction. The abnormal results with metals and hydrogen are either due to experimental error or to some unexplained, and therefore interesting, reaction.

On p. 333 it is stated that copper in steel retards corrosion. It would have been more accurate to have said that it retards atmospheric corrosion. It is not claimed nowadays that copper protects steel in the presence of a solution. On p. 334 the author comments on the fact that manganese steel is so hard that it can scarcely be drilled and yet at the same time so soft that it can be dented by a hammer. Howe's explanation of this apparent discrepancy should have been given.

Apart from these few slips, the book is admirable and contains an immense amount of information. The data in regard to the physical properties of the pure metals and to the effect of impurities on them are extremely valuable. The different constitution diagrams for pairs of alloys are extremely satisfactory. The treatment of steel and cast iron is very elaborate. The reviewer does not happen to believe that ferrite and graphite are the stable phases at ordinary temperatures; but the author very properly gives the views of the metallurgists. The chapter on the special steels is good and the reviewer was interested in Le Chat-

elier's summary, p. 432, written in 1904. "The purpose of the addition of the special elements is to increase the toughness. It is quite possible to produce high tensile strength in carbon steel; but only by adding a special element is it possible to secure the combination of high tensile strength, ductility, and toughness. This increased toughness can be utilized in three different ways. (1) Parts can be made appreciably lighter, maintaining at the same time the same strength and toughness. This is of particular importance in the automobile industry where weight is such an important factor. The cost of production may also be reduced, due directly to the lower weight of the parts to be handled. (2) Maintaining the same weight and toughness, the parts can be loaded more heavily, which lessens the danger of over-loading and severe straining. (3) Maintaining the same weight and strength, much greater toughness can be secured, which lessens materially the liability of failures and, therefore, of serious accidents or delays." *Wilder D. Bancroft*

A Dictionary of Applied Chemistry *By Sir Edward Thorpe. Vol. II. 23 × 17 cm; pp. viii + 717. New York and London: Longmans, Green and Co., 1921. Price: $20.00.*—The second volume of this important work appeared with commendable promptness. Some of the interesting items are: camphor, candles, carbohydrates, carbolic acid, carbon, carborundum, casein, castor oil, catechu, celluloid, cellulose, cement, cerium, cheese, chemical affinity, chloral, chlorine, chloroform, chromium, cider, cinchona alkaloids, citric acid, clay, cobalt, cochineal, cocoa, coffee, coke, colloids, colorimeter, color, columbium, copper, corrosion, creosote, cryoscopy, crystallization, cyanides, decolorizing carbons, desiccation, diamond, diazocompounds, diazo and tetrazo coloring matters, disinfectants, distillation, dyeing, electrodeposition, enamels, ergot, esterification, evaporation, explosion.

It is interesting to note that in 1903 the European production of candles was not under 300,000 tons. Under carbon there is no explicit statement, p. 61, that carbon cannot be oxidized to mellitic acid. It is inaccurate, p. 63, to quote from Cabot that "when produced from the natural gas in American oil wells, the carbon black differs from ordinary lamp-black by mixing with water on being shaken with it; ordinary lamp-black will not do this." It is not a question of carbon but of cleanliness. Carbon black, though not very clean, is usually cleaner than lamp-black and therefore mixes more readily with water. The use of chloropicrin in the war was certainly important enough to warrant mention, p. 227.

Under diamond, p. 300, we read that "the diamond-bearing rock of the Transvaal Mines fills volcanic pipes, 200–300 yards (in the case of the Premier mine half a mile) across, penetrating vertically the surrounding beds of basalt, shale, diabase, and quartzite, and extending to unknown depths. The rock, known as kimberlite, or locally as 'blue ground,' consists mainly of a hydrated magnesium silicate with much the same composition as serpentine. It contains boulders and broken fragments of various rocks (basalt, shale, sandstone, quartzite, granite, mica-schist, eclogite, etc.), and minerals (ilmenite, pyrope, enstatite, chrome-diopside, iron pyrites, etc.), and is of the nature of a volcanic agglomerate. Diamond is present in this rock on an average of one part in forty millions, and in the richest part of the Kimberley mine one part in two

millions. Numerous pipes of a similar character, but containing few or no diamonds are scattered over a wide area in South Africa. The diamond was brought up from below with the igneous material, which must have been derived from a basic magma rich in olivine. Although the origin of diamond has been the subject of much discussion, there seems no reason to doubt but that it crystallized from this basic magma. The rare presence of diamonds embedded in boulders of eclogite (a garnet-pyroxene rock) found in the blue ground has led to the suggestion that this is the mother-rock; but it is quite conceivable that the mineral crystallized from more than one kind of basic magma."

Under dyeing, p. 574, we find that "the precise cause or causes of the different behavior of the textile fibres in dyeing is still a matter of uncertainty; but there is little doubt that the chemical and physical properties both of the fibre and of the dyestuff are all factors of the complicated phenomena of dyeing. . . . A full discussion of the evidence for and against the mechanical and chemical theories of dyeing cannot be here entered upon; but a general review indicates that the attempt to cover all dyeing phenomena by any one simple explanation must fail, and that many factors are concerned, the relative importance of which varies in different cases. In the dyeing of wool or silk with acid or basic dyes, it may be taken as established that chemical combination occurs; but prior to this some hydrolysis of the fibre and more or less complete ionization of the dyestuff takes place. Surface concentration of the dye on the fibre probably also occurs, and the coagulation and precipitation of the dissociated colloidal dyestuff also plays a part. . . . In the case of the dyeing of vegetable fibres, the same factors probably operate, but their relative importance is not the same, the physical factors—precipitation, surface attraction, and osmosis—predominating over the effect of direct chemical action."

The classification of dyes adopted in this article is: (1) mordant dyes; (2) acid-mordant dyes; (3) acid dyes; (4) direct dyes; (5) basic dyes; (6) sulphide dyes; (7) vat dyes; (8) ingrain dyes. *Wilder D. Bancroft*

A Text-Book of Inorganic Chemistry. *Edited by J. Newton Friend. Vol. IX, Part I. 23 × 17 cm; pp. ix + 367. London: Charles Griffin and Co. Ltd.; Philadelphia: J. B. Lippincott Co., 1920. Price: $6.00.*—In the preface it is stated that owing to the importance of iron, it would not be taken up in the logical order but that Part II of this volume would be assigned to it. Since the platinum metals are so closely similar in many of their properties, it was decided to treat of their detection and estimation all together rather than to deal with each separately at the end of the chapters devoted to their compounds. The chapters are entitled: general characteristics of the elements of group VIII; cobalt; nickel; ruthenium; rhodium; palladium; osmium; iridium; platinum; detection and estimation of the platinum metals.

On p. 29 is the statement that "Neumann and Streintz observed that repeated oxidation and reduction of cobalt oxide tends to diminish the power of cobalt to occlude hydrogen. As Baxter has pointed out, this is probably due to the fact that these operations tend to render the cobalt increasingly compact." This is rather surprising because repeated oxidation and reduction of copper increases its catalytic power very much.

The reviewer is of the opinion that Browne's electrolytic process for sep-

arating copper and cobalt has not been worked in Canada for a number of years, the International Nickel Company having substituted the Orford process for it.

The reviewer was interested in the statement, p. 119, that "nickel sulphide may also be obtained by precipitation from solutions of nickel salts. It then occurs in three different polymeric forms, α, β, and γ, according to circumstances. Of these, α-nickel sulphide is soluble in dilute mineral acids, even with as low a concentration as 0.01 normal. β-nickel sulphide dissolves easily in 2-normal hydrogen chloride, whilst γ-nickel sulphide is insoluble unless oxidizing agents are present." One would like to see that work checked very carefully so as to be certain that these are real modifications.

The author calls attention, p. 185, to the fact that a quantity of aniline is produced when hydrogen is passed through an alcoholic solution of nitrobenzene after the addition of some palladium hydrosol. The interesting thing is that aniline is a poison to colloidal platinum when catalyzing hydrogen peroxide. This should be studied, though it is quite possible that it is the alcohol or the nitrobenzene which changes the conditions.

The experiments of Sieverts on the increasing solubility of hydrogen in platinum with rising temperature are mentioned, p. 265; the phenomenon apparently does not worry anybody except the reviewer. On p. 271 are given data by Gröh which illustrate in a striking manner that increasing the stability of platinum black or adding gelatine cuts down markedly the catalytic action of the platinum or hydrogen peroxide. The reviewer confesses with shame that he had forgotten these figures absolutely. On p. 274 it is stated that platinum black converts hydrazine into ammonia and nitrogen. There is nothing to show what the intermediate steps are.

The author quotes from Harbeck and Lunge to the effect that "platinum black absorbs slowly sixty times its volume of carbon monoxide at ordinary temperature, and appears to form a chemical compound with it, although efforts to isolate any such substance have hitherto proved abortive. The adsorption can hardly be a purely mechanical effect, since other gases such as hydrogen do not effect its elimination. Upon heating to 250° C the carbon monoxide is liberated suddenly." Nobody would guess that this represents a view-point of over twenty years ago and that today it would be a rash man who would question the adsorption of carbon monoxide by platinum.

Interesting things that somebody will have to tackle some day are the trichroism of ammonium platinocyanide, p. 319, the blue reflex of cerium platinocyanide, and the green reflex of yttrium platinocyanide.

The volume is a good one so far as presentation of facts is concerned but it is not inspiring at all. The author has evidently refrained conscientiously from calling attention to research problems. One can admire the way in which he has stuck to his principles without endorsing the latter.

Wilder D. Bancroft

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